NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT

NsG-657/11-02-018

GEORGIA INSTITUTE OF TECHNOLOGY

SEMIANNUAL REPORT

September 15, 1967 to March 14, 1968

Report Prepared By

A. L. Ducoffe and V. Crawford

Co-chairmen of

Georgia Tech Space Sciences Technology Board

August 15, 1968

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

Office of
The Vice President for
Academic Affairs

August 15, 1968

Dr. Francis B. Smith
Assistant Administrator for
University Affairs
National Aeronautics and Space
Administration
Washington, D. C. 20546

SUBJECT: Semiannual Report
September 15, 1967 to March 14, 1968
Multidisciplinary Research Grant NsG-657/11-02-018

Dear Dr. Smith:

The Georgia Institute of Technology Space Sciences and Technology Board is pleased to submit herewith thirty (30) copies of a semiannual report for Multidisciplinary Research Grant NsG 657/11-02-018.

We shall be pleased to provide any additional information that you find necessary.

Sincerely yours,

W. L. Bloom
Acting Vice President for
Academic Affairs

WLB/rs

Enclosures

cc: Dr. E. D. Harrison
Mr. H. L. Baker
Members of the Space Sciences and Technology Board

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GEORGIA INSTITUTE OF TECHNOLOGY

I. SUMMARY

The National Aeronautics and Space Administration granted the Georgia Institute of Technology $600,000 on June 15, 1964, $300,000 on June 15, 1965, $300,000 on March 15, 1966, and $300,000 on March 15, 1967 for the support over five years and nine months of basic scientific research entitled "Multidisciplinary Research in the Space Sciences and Technology."

The grant funds have been used for the first four periods to support an expansion of multidisciplinary research programs in materials and materials processing, transport phenomena, energy conversion, systems, and nuclear processes.

The grant has been administered by the Space Sciences and Technology Board established at the Georgia Institute of Technology. The Co-chairmen of the Board are Dr. A. L. Ducoffe, Director of the School of Aerospace Engineering, and Dr. V. Crawford, Director of the School of Physics. The other Board members are H. F. Bauer, Engineering Mechanics; C. H. Braden, Physics; W. O. Carlson, Mechanical Engineering; W. B. Jones, Electrical Engineering; R. H. Kasriel, Mathematics; H. A. McGee, Jr., Chemical Engineering; and W. M. Spicer, Director, School of Chemistry.

The fourth grant period runs from March 15, 1967 through March 14,1968. The present document reports the research results obtained during the second six months of this period.

An indication of the research activity stimulated by the grant during this reporting period is the publication in recognized journals of 11 papers, the acceptance of 5 others, and the submission of 2 additional. Three papers have been read at scientific meetings.

A proposal for continued support was submitted to the National Aeronautics and Space Administration in October, 1967. It has been funded at a reduced rate.

II. RESEARCH RESULTS

A. MATERIALS AND MATERIALS PROCESSING

1. Preparation of New and Unusual Complex Metal Hydrides - E. C. Ashby

The objectives of this program are to establish methods for the preparation of complex metal hydrides, e.g., $Mg(AlH_4)_2$, Li_3AlH_6 and Li_2MgH_4 which could be used as high energy solid rocket propellants.

$\underline{Mg(AlH_4)_2}$

Although reaction of $LiAlH_4$ and MgI_2 forms $IMgAlH_4$ in diethylether, $Mg(AlH_4)_2$ is produced in tetrahydrofuran.

$$LiAlH_4 + MgI_2 \xrightarrow{Et_2O} IMgAlH_4 + Li$$

$$2LiAlH_4 + MgI_2 \xrightarrow{THF} Mg(AlH_4)_2 + LiI$$

The above results are obtained regardless of the amount of $LiAlH_4$ used in excess. The reason for this result can be explained by the fact that $IMgAlH_4$ disproportionates in tetrahydrofuran.

$$2IMgAlH_4 \xrightarrow{THF} MgI_2 + Mg(AlH_4)_2\downarrow$$

The disproportionation of $IMgAlH_4$ to $Mg(AlH_4)_2$ and the direct reaction of MgI_2 and $NaAlH_4$ in THF provide the best methods available for making $Mg(AlH_4)_2$.

$\underline{M_3AlH_6}$

Although aluminum powder containing 1% titanium proved very effective for aluminum-hydrogen reactions with ethylene, this type of aluminum proved to be very poor for reaction with alkali metal hydrides to form M_3AlH_6 compounds. A method of activating Al powder was found that resulted in facile reaction of Al, H_2 and an alkali metal hydride.

$$3Na + Al + 3H_2 \longrightarrow Na_3AlH_6$$

After successful conditions for preparing Na_3AlH_6, were established, attempts were made to prepare other alkali metal hexaaluminohydrides, e.g., K_3AlH_6 and Li_3AlH_6. K_3AlH_6 was successfully prepared in a pure state from K, Al and H_2, however the preparation of Li_3AlH_6 from Li or LiH, Al and H_2 was unsuccessful.

$\underline{Li_2MgR_4}$

Compounds of the type Li_2MgR_4 have been prepared where R = Me, Et, Bu and Ph by reaction of the corresponding lithium alkyl with the magnesium alkyl in ether.

$$2LiR + MgR_2 \rightleftharpoons Li_2MgR_4$$

However the resulting product does not appear to be stable in solution and is actually in equilibrium with its component parts. Efforts are being made to prepare these compounds in hydrocarbon solvent in order to increase the stability which may come about through non-solvation of the product.

2. Effects of Viscous and Inertia Type Damping on Beams and Plates - J. R. Baumgarten

During the period September 15, 1967 through March 14, 1968 a digital computer program was written and preliminary runs were made. Concurrently, experimental apparatus was constructed and was in the process of being set-up by a Ph.D. student at the end of the grant period.

After March 14, 1968 the analysis will be extended to plates to cover energy dissipation in viscoelastic coated plates. The research after March 14, 1968 will be supported by Georgia Tech.

3. Fatigue Failure Due to Random Vibration - M. C. Bernard

Using Miner's criterion as a starting point, the calculation of fatigue damage has been hampered by the present unavailability of the necessary probability density functions to evaluate the damage of a structure in a random environment. Only a few trivial situations have been investigated in the past. Here the vast amount of work on the analysis of the extremal statistics of normal random processes, in particular by Rice,[1] has been used to develop analytical expressions for the life and probability of failure of a structure under both narrow and broad-band loading.

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[1] Rice, S. O., Mathematical Analysis of Random Noise, Bell System Tech Journal, Vol. 23, 24, 1945.

In the analysis described above, due to the complexity of the problem, simplifying assumptions and approximations have had to be employed. A program of tests is now being investigated to check the expressions designed for life under narrow and broad-band loading and for probability of failure. In particular it is hoped to determine the effect of varying the shape of the power spectrum and to check the application of the expressions derived for probabilities of failure.

During the period covered by this report a short paper on the initial stages of this work has been accepted for publication in the Journal of the Acoustical Society. A more comprehensive report is currently being prepared for submission at a later date.

4. Jahn-Teller Effect in Transition Metal Complexes -

J. A. Bertrand

A study of the effect of temperature on the Jahn-Teller distortion of low-spin cobalt(II) in order to verify the prediction of a transition from a dynamic effect to a static effect.

Previous work at room temperature indicated either no Jahn-Teller distortion or a dynamic Jahn-Teller distortion; to decide between these possibilities, the structure of an analogous nickel(II) compound was determined. Comparison of the temperature parameters for $K_2BaCo(NO_2)_6$ and $K_2BaNi(NO_2)_6$ indicated much larger thermal motion for the nitrite groups of the cobalt compound; since this was the only difference in the two structures and since nickel(II) is not susceptible to Jahn-Teller distortions, the results are consistent with a dynamic or vibrational Jahn-Teller effect for cobalt(II).

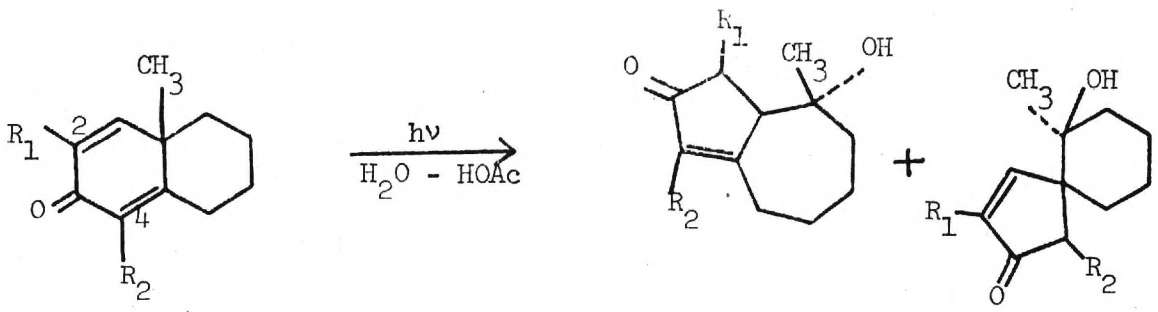
Diffraction studies as a function of temperature indicated a transition from cubic to orthorhombic at -10°C; the unit cell was compressed along two axes, to 10.51 A, and elongated along the third axis, to 10.86 A,

in the transition from the cubic form, which had a unit cell parameter of 10.66 A. Cobalt - nitrogen distances of 1.89, 1.90, and 2.10 A. confirm a static distortion below the transition temperature.

Publications: Paper presented at the Southeastern Regional Meeting of the American Chemical Society, Atlanta, Georgia, November, 1967: "Jahn-Teller Distortions: Low Temperature Studies of $K_2BaCo(NO_2)_6$."

5. Photochemistry of Cylohexadienones - D. S. Caine III

The influence of substituents at C-2 and C-4 on the course of photochemical rearrangements of 6/6-fused cross-conjugated cyclohexadienones of type I in aqueous acetic acid have been investigated in detail.



I II III

a. $R_1 = R_2 = H$

b. $R_1 = CH_3$, $R_2 = H$

c. $R_1 = H$, $R_2 = CH_3$

d. $R_1 = CO_2H$, $R_2 = H$

e. $R_1 = CO_2CH_3$, $R_2 = H$

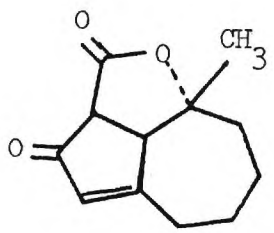
f. $R_1 = H$, $R_2 = CO_2CH_3$

g. $R_1 = H$, $R_2 = CN$

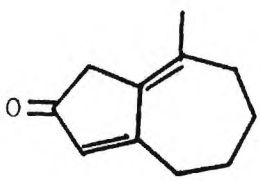
h. $R_1 = OCH_3$, $R_2 = H$

i. $R_1 = H$, $R_2 = OCH_3$

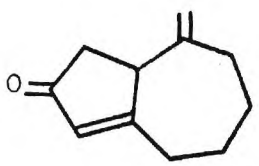
Irradiation of Ia gave a mixture of the 5/7-fused hydroxy ketone IIa and the spiro hydroxy ketone IIIa in low yield and in approximately equal amounts. Phenolic materials were the major products of this reaction. Similar results have been obtained for a derivative of Ia having an unsubstituted A ring.[1] It was known that the methyl substituted dienones Ib and Ic gave good yields of the IIIb and IIc, respectively, under similar conditions.[2,3] Significant quantities of phenols were not obtained from the methyl substituted systems. Dienones Id and Ie, having electron withdrawing substituents at C-2, led mainly to IIa (resulting from decarboxylation of the unstable IId) and IIe in the same media.[4] Interestingly, Id also gave the lactone IV and the dienones V and VI in varying proportions in a variety of media.[4] Attempts to prepare the dienone If, having a carbomethoxyl grouping at C-4, did not lead to pure products; but the related nitrate Ig was easily obtained. On irradiation in aqueous acetic acid it gave IIIg as the only identifiable product in good yield. The methoxy dienones Ib and Ii have been prepared. Irradiation of Ih gave IIIh in good yield and no other identifiable products. Work on the dienone Ii is incomplete at this point.



IV



V



VI

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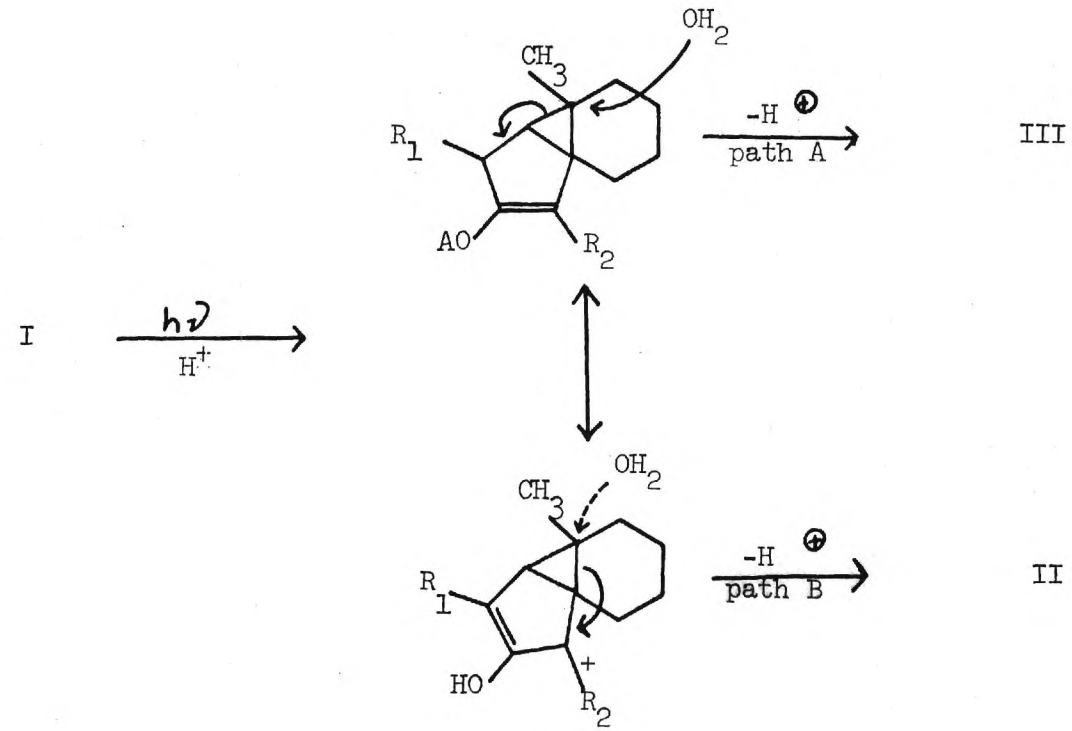
1 P. J. Kropp and W. F. Erman, J. Am. Chem. Soc., 85, 2456 (1963).

2 P. J. Kropp, ibid., 86, 4055 (1964).

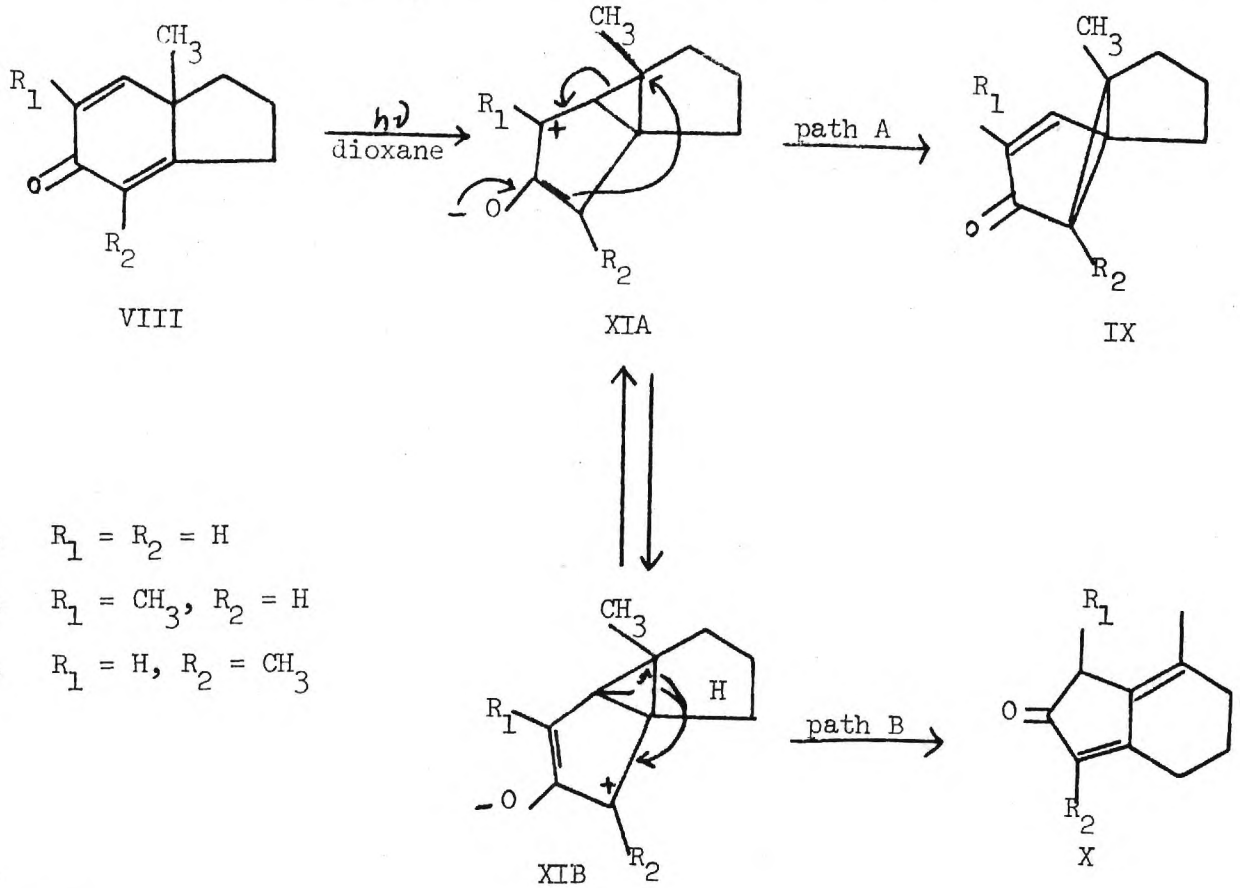
3 (a) D. Caine and J. B. Dawson, J. Org. Chem., 29, 3108 (1964); (b) P. J. Kropp, ibid., 3110 (1964)

4 D. Caine, J. F. Debardeleben, Jr., and J. B. Dawson, Tetrahedron Letters, 3629 (1966).

The observed substituent effects can be rationalized in terms of the hypothetical intermediate VII. In those cases (Ib and Ih) in which electron releasing groups are present at C-2 on the dienone chromophore VIIA would be expected to be favored and path A cleavage is the observed course of the reaction. Also, with Ig, having an electron withdrawing group at C-4, VIIA would be expected to be favored and path A cleavage obtains. With Ic resonance structure VIIB would be expected to be favored and path B cleavage is the exclusive pathway of reaction. Also, with Id and Ie path B cleavage is expected and observed. This work clearly shows that the cross-conjugated cyclohexadienone system has a high propensity for rearrangement regardless of the electronic nature of the substituents present. The work also demonstrates that photochemical rearrangements of compounds of the type I can provide a convenient method of synthesis of substituted 5/7-fused and spirocyclic compounds which would be difficult to obtain by thermal methods. Most of the above work has been covered in earlier reports.



During the period of September 15, 1967 to March 14, 1968 attention was directed to the synthesis and a study of the photochemical behavior of the 6/5-fused cyclohexadienones VIIIa-c. These compounds were irradiated in anhydrous dioxane at 2537Å. The major products of the reaction in all cases were the bicyclo[3.1.0]hex-3-en-2-ones IXa-c. The linearly conjugated dienone Xa was also obtained from VIIIa. The IXa/Xa ratio was 5:2. A trace of Xc was also isolated on irradiation of VIIIc, but no Xb could be isolated from VIIIb. The behavior of VIIIa-c resembles closely that of Ia-c under the same conditions, but differs markedly from that of B-nor-1-dehydrotesterone acetate,[5] the only other 6/5-fused cross-conjugated dienone studied so far. The steroidal dienone gives exclusively a 5/6-fused linearly conjugated system related to Xa on irradiation of 2537Å in dioxane. The formation of IX and X from VIII may be considered to involve a hypothetical intermediate such as XI.



a. $R_1 = R_2 = H$

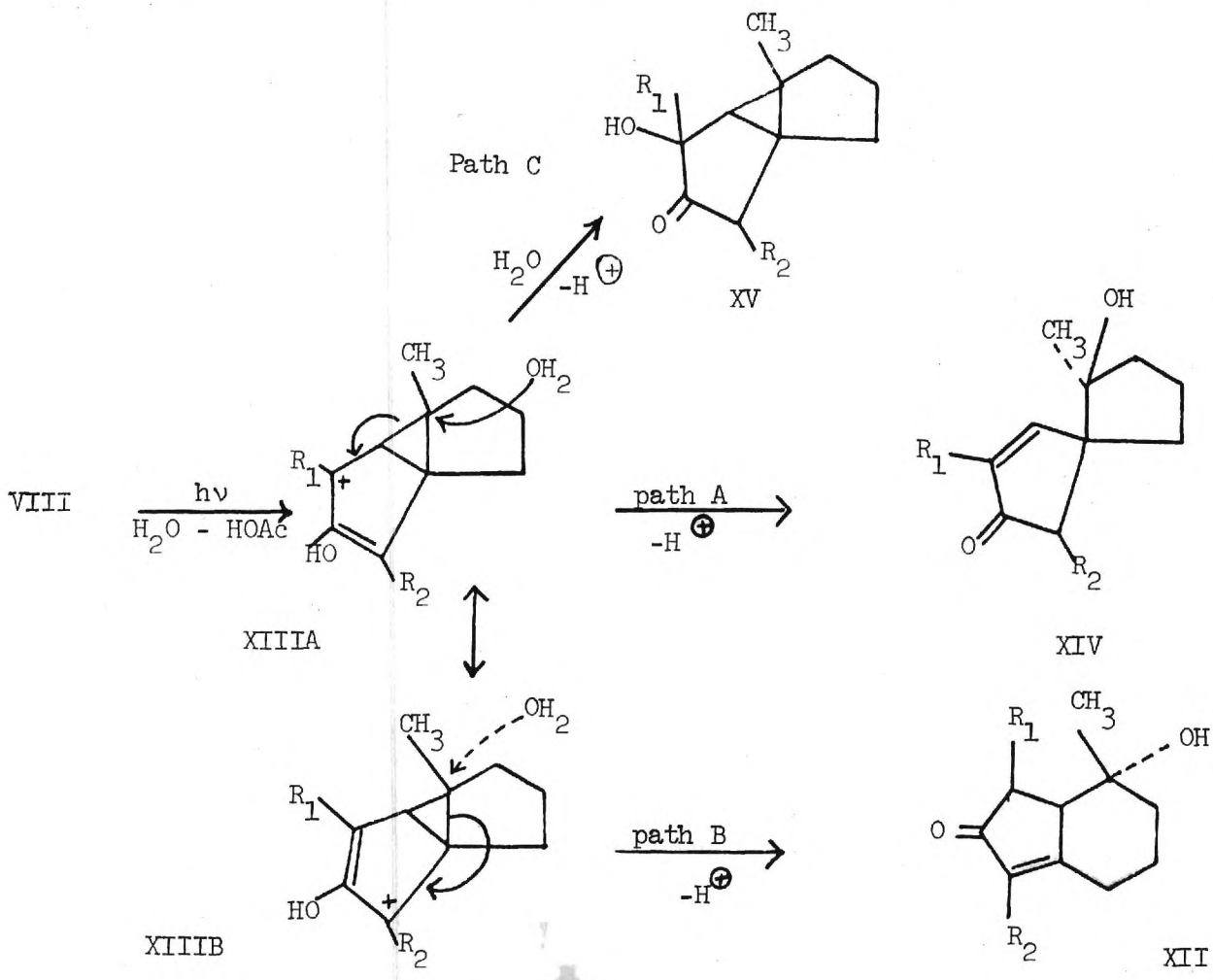
b. $R_1 = CH_3$, $R_2 = H$

c. $R_1 = H$, $R_2 = CH_3$

[5] G. Bozzato, H. P. Throndsen, K. Schaffner, and O. Jeger, J. Am. Chem. Soc., 86, 2073 (1964).

Thus it appears that path A reaction is preferred for the simply bicyclic systems such as VIII, but added strain which would result from the trans fusion of ring C to a system such as IX causes the intervention of path B in the steroid case. The presence of methyl substituents clearly favors the formation of IX relative to X. The yields of the tricyclic products IX were of the order of 50% in all runs.

The photochemical behavior of VIIIb and VIIIc in aqueous acetic acid has also been studied. Dienone VIIIc was found to behave in a manner similar to Ic under these conditions. It gave the hydroxy ketone XIIc in about 50% yield along with a trace of the acetate derivative of XIIc on irradiation in 45% acetic acid using a Pyrex filter. XIIc appears to arise by path B cleavage of the mesoionic cyclopropyl intermediate XIII. This be-



havior is expected since the methyl group at C-2 should favor XIIIB. It was anticipated that VIIIb would lead to the spiro compound XIVb via path A cleavage of XIII. However, on irradiation of VIIIb in aqueous acetic acid no XIVb could be isolated, but XIIb and a product having a structure tentatively assigned as XVb were isolated in 40 and 20 per cent yields, respectively. It appears that even though XIIIA should be favored when a methyl group is present at C-2, path A cleavage is an unfavorable process in this system. Unusual strength of the 1,9-bond as a result of a high degree of s character because it is fused exocyclically to two five membered rings is a possible explanation for path B and path C being the only modes of reaction of VIIIb.

Work on the behavior of VIIIa in aqueous acetic acid and on the photochemical behavior of systems of the type IX in a variety of media is in progress.

6. A Study of Creep Induced Instability - R. L. Carlson

Analytical and experimental results were obtained under the program and these will be described in the sections below.

Analytical Results: The definition of a stable inelastic material proposed by Drucker[1] was extended to apply to a structural element. Drucker's definition states that the following relation must be satisfied for a homogeneously stressed body to be stable:

$$\int_{t_1}^{t} \left(\sigma_{ij}^{(2)} - \sigma_{ij}^{(1)}\right)\left(\dot{e}_{ij}^{(2)} - \dot{e}_{ij}^{(1)}\right) dt \geq 0 . \qquad (1)$$

In this equation the σ_{ij} and $\dot{e}_{ij}$ terms are, respectively, the stress and strain rate components, and integration extends from the time at which an inspection of stability begins, $t = t_1$, to some time $t > t_1$. The superscript 1 refers to a basic state and the superscript 2 refers to any admissible neighboring state.

To investigate the applicability of this criterion to structural elements, it is necessary to integrate Eq. (1) over an element which in general will not be homogeneously stressed. To correlate with the experimental program, a compressively loaded column was selected as a basis for developing the required analysis. The following criterion for stability was developed for this case:

$$-\int_{t_1}^{t}\int_{o}^{L} \left(M_2 - M_1\right)\left(\dot{K}_2 - \dot{K}_1\right) dx\, dt \geq 0 . \qquad (2)$$

---

[1] D. C. Drucker, Journal of Applied Mechanics, Vol. 26, Series E, 1959, pp. 101-106.

Integration now extends over the column length, L, and M and $\dot{K}$ are, respectively, the bending moment and the rate of change of curvature with respect to time.

An investigation of stability in the small can be made by expanding the bending moment and rate of curvature change about the inspection time $t = t_1$ and then making an examination of the expansion as $t \to t_1$. If the lowest order term is present for the existing conditions, its sign determines stability. If the lowest order term vanishes, the next higher order term must be examined.

To include all effects which may be of interest it is desirable to consider the bending moment $M = Pv$ to vary with both axial load P and lateral deflection v. Thus, for example,

$$\dot{M} = \dot{P}v + P\dot{v} .$$

From these results it is apparent that the stability examination must include a knowledge of how both P and v change with time. Since a given program of loading for P will produce a corresponding history for v, and vice versa, this relationship must be established for each column of interest. An analysis of this relationship, which involves the constitutive law for the column material, is being continued.

Experimental Results: The objective of the experimental program was to design apparatus and specimens for conducting experiments in which the effect of creep strain history on column behavior could be studied. The design of a fixture which restricts column strain to uniform compression for a controlled period of time and, upon release, frees the column for lateral deflection was completed, and the apparatus was made in the Aerospace Engineer-

ing machine shop.

The apparatus has been used to conduct column stability inspections, and has been found to impose the conditions required prior to inspection. The deflection measurement system is not, however, sufficiently sensitive to provide the type of quantitative data desired, and alternate methods of measurement and being considered.

7. The Growth of Nonmetallic Single Crystals Using the Internal Centrifugal Zone Technique - A. T. Chapman

The growth of nonmetallic single crystals using the "Internal Centrifugal Zone" technique (a modified floating-zone procedure) was the long range objective of this project. Intermediate goals included the acquisition of high frequency induction generators, and the screening and selection of the refractory oxides which exhibit sufficient electrical conductivity at elevated temperatures to sustain eddy current heating; and permit internal melting and crystal growth.

Since the last report period a 30 mc induction generator has been acquired and set up, and melting experiments have been conducted on a number of oxides using this unit. The following oxides have been successfully melted: lime and magnesia stabilized ZrO_2, TiO_2, $Fe_2O_3(Fe_3O_4)$, and UO_2. Figure I shows longitudinal section of a 20 mm diameter ZrO_2 + 5% CaO specimen containing a transparent solidified interior which was melted above 2700° C ($\sim$ 5000° F). The segregation of impurities at the top of the molten zone occurred in this experiment.

Additional equipment to provide the mechanical motion (rotation and vertical travel) necessary to grow a single crystal, instead of the polycrystalline interior displayed in Figure I, is currently being constructed in conjunction with the oxide-metal composite project, also supported by NASA.

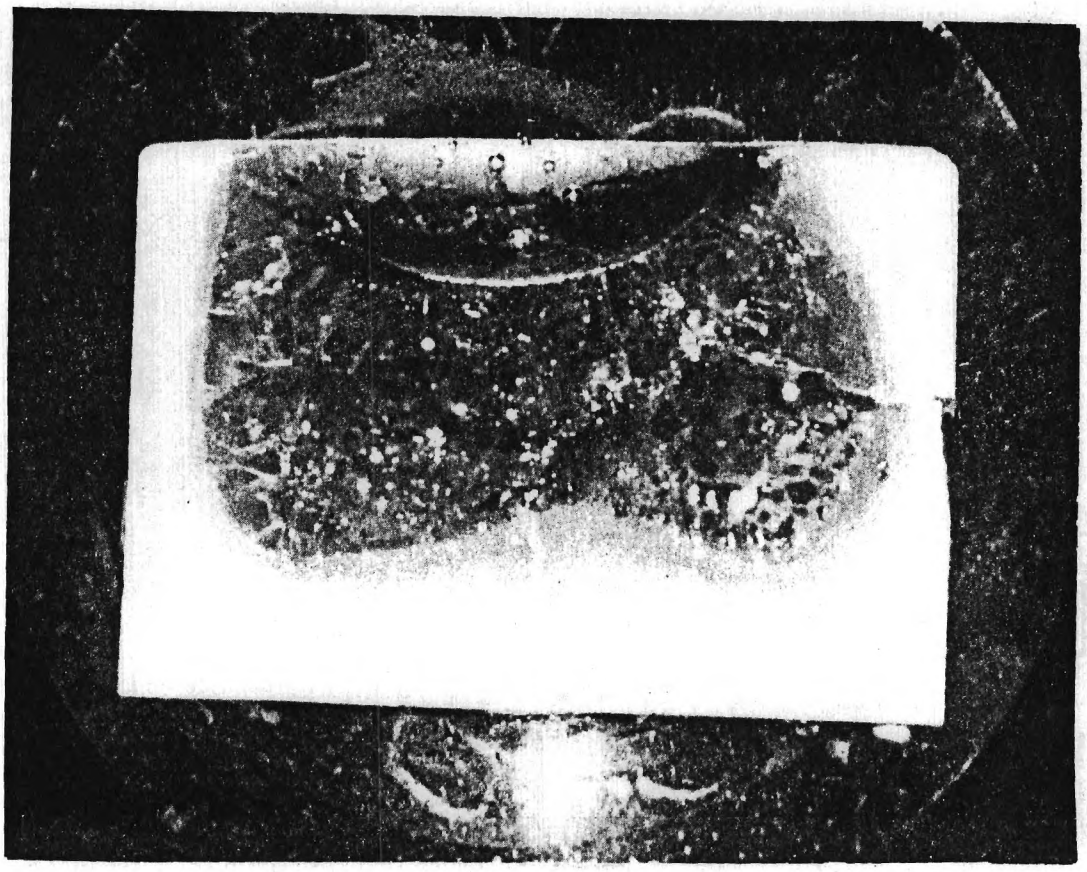


Figure I. Longitudinal section of centrally melted ZrO_2 + 5% CaO pellet containing small transparent crystals. Mag. 6X

8. The Measurement of Surface Deformations by Using Lasers to Produce Holographic Contours - R. M. Dinnat

As mentioned in the progress report for the first half of the grant period, holographic contouring was abandoned as a practical laboratory method for measuring the displacements of structural models used in Civil Engineering work; reasons for this decision were given in the report.

The latter half of the grant was spent investigating the feasibility of a proposed technique that utilizes the laser's capabilities as an intense light source. The laser, in conjunction with a fan lens, is used to cast a line of light on the model. Changes in the shape of the model along the line of light are determined by parallax measurements.

The technique proved to be theoretically feasible, and the remaining funds were used to purchase a small laser and a fan lens with which to begin some simple experiments for determining the accuracy of such measurements.

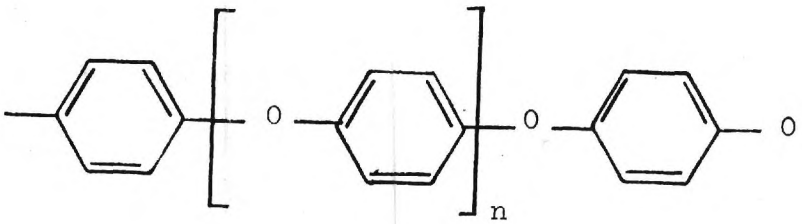
The period of the grant expired prior to the arrival of the laser and the fan lens.

9. Chemistry Fundamental to Resistant Polymer Development - C. L. Liotta

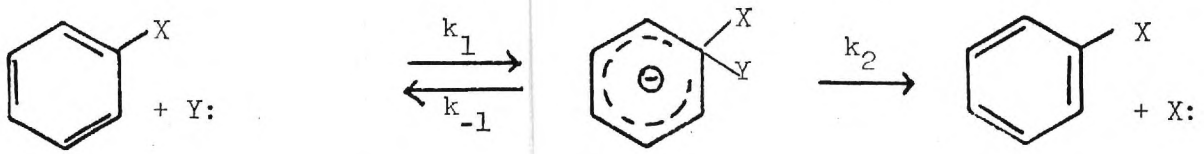
Objectives: The objectives of this research project are:

(1) To learn whether the presence of hydroxyl groups on an aromatic ring facilitates nucleophilic displacement of a halide ion attached to the same ring, and

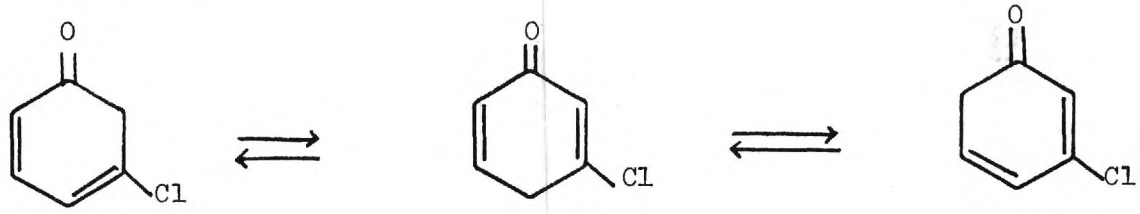
(2) To relate this chemistry to the development of resistant polymers of the polyphenyl ether type:



Introduction: The commonly accepted mechanism for aromatic nucleophilic substitution involves the following addition-elimination sequence:



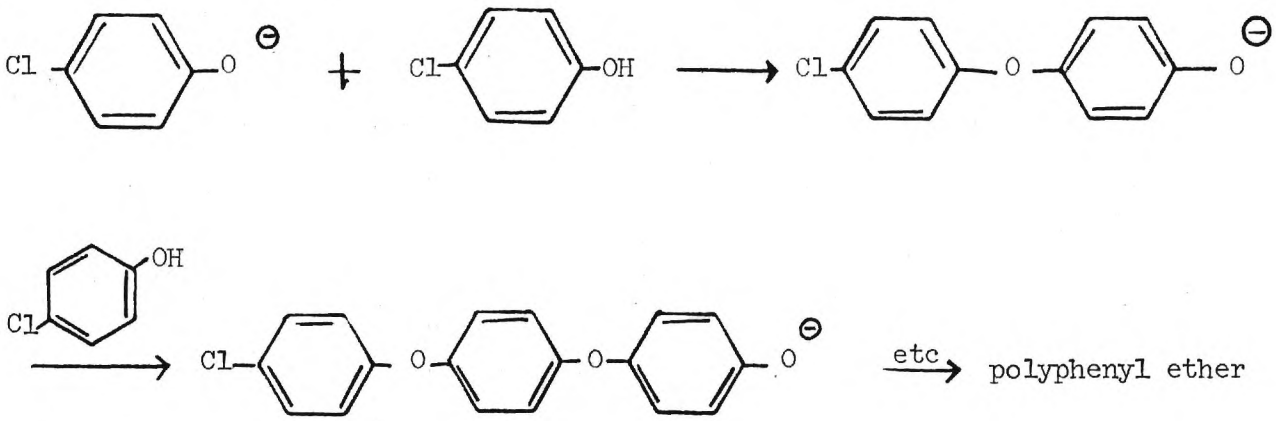
It has been found that electron-withdrawing groups on an aromatic ring, such as nitro, markedly activates the halogen of the aryl halide toward displacement. It was anticipated, however, that a hydroxyl group would also activate an aryl halogen but in quite a different manner. As an example, it is convenient to consider m-chlorophenol. At high temperatures and in protic solvents the following forms of this compound may be present in moderate concentrations:



A B C

A, B and C are nothing more than the ketonized forms of the enol m-chlorophenol, but unlike m-chlorophenol the halogen should be quite reactive toward nucleophiles

since all three forms are vinylogs of acid chlorides. Carrying over the same reasoning one can anticipate the following reaction sequence when the nucleophile p-chlorophenoxide ion is reacted with p-chlorophenol:



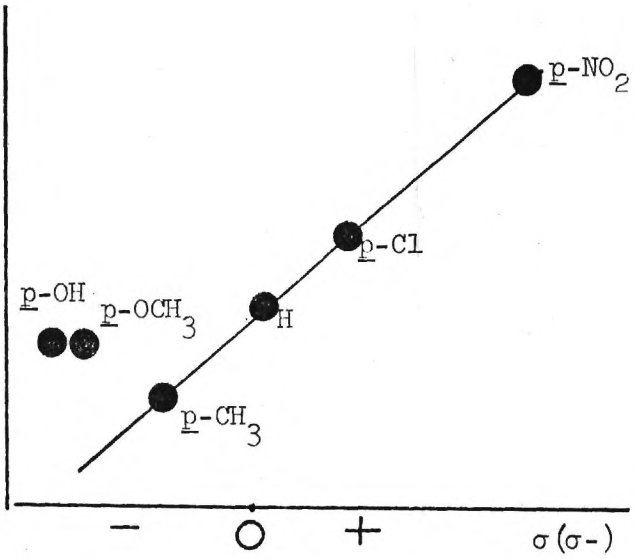
Plan of Attack: In order to determine if there is an enhancement of rate with halophenols due to this ketonization mechanism, the nucleophile piperidine was reacted with a series of substituted halobenzenes. By plotting to "correct" substituent constant against the log of the second-order rate constant, a linear free energy (Hammett) plot could be constructed. If the halophenols were indeed activated by a ketonization mechanism, the rate enhancement should be shown by the point for the halophenol lying substantially above the line.

Results and Discussion: The first series of compounds studied were the para-substituted chlorobenzenes. The reactions were carried out in tri-ethyleneglycol solvent at 244.5° using piperidine as the nucleophile. Table I summarizes the data obtained. Figure I shows a plot of log k vs σ-constants.

Table I

Substituent	$k(M^{-1})(hr^{-1})$
NO_2	2.7
Cl	4.44×10^{-3}
	4.42×10^{-3}
H	9.04×10^{-4}
	11.01×10^{-4}
CH_3	3.03×10^{-4}
OCH_3	1.24×10^{-3}
OH	1.15×10^{-3}
	1.38×10^{-3}

Figure I



The results with the para-substituted chlorobenzenes appear to indicate that there is marked rate enhancement in the reaction of piperidine with p-chlorophenol. The nature of this rate enhancement, however, is still not known with certainty. It could be due to the theorized ketonization mechanism or perhaps to something else. To decide this issue, the reaction kinetics of many more substituted chlorobenzenes (especially the meta-substituted chlorobenzenes) must be investigated along with detailed product analysis of the reaction mixtures.

It was of interest to determine the relative ease of displacement of the various halides from unactivated benzene. Table II shows the results of the reaction of fluorobenzene, chlorobenzene, bromobenzene and iodobenzene with piperidine in triethyleneglycol solvent at 239.5°.

Table II

Substituent	$k(M^{-1})(hr^{-1})$
F	1.12×10^{-2}
	1.07×10^{-2}
Cl	1.59×10^{-3}
	1.93×10^{-3}
Br	1.47×10^{-2}
	1.36×10^{-2}
I	2.13×10^{-2}
	2.57×10^{-2}

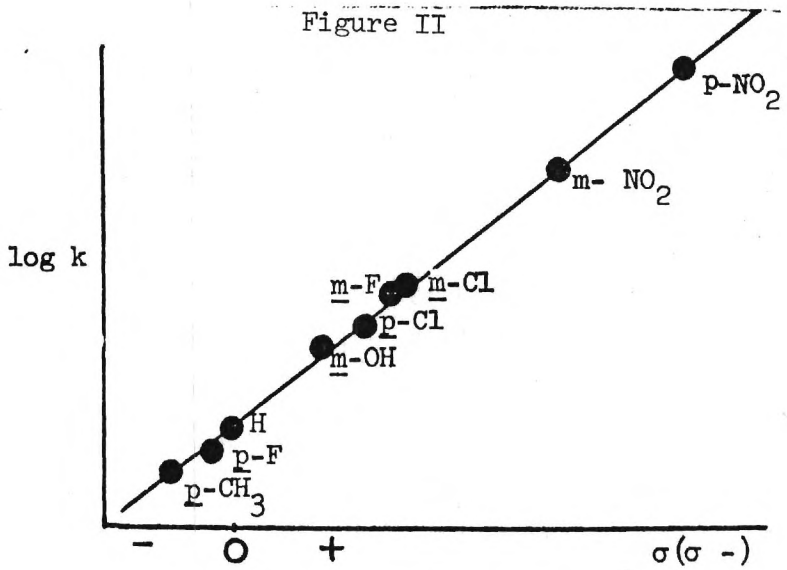
The results clearly indicate the following order of halogen displacement: Cl < F < Br < I.

Since fluorine is much more easily displaced than chlorine, it was anticipated that substituted fluorobenzenes would undergo aromatic nucleophilic displacement at reasonable rates at temperatures lower than 244.5° thus avoiding much of the tar observed in the reaction of substituted chlorobenzenes. Table III shows the results of the reaction of a series of meta- and para-substituted fluorobenzenes with piperidine in triethyleneglycol solvent at 195°. Figure II shows a plot of log k vs σ-constants.

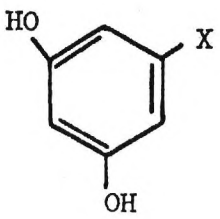
Table III

Substituent		$k(M^{-1})(Hr^{-1}$	
m-Ch_3	7.77×10^{-4}	8.28×10^{-4}	7.64×10^{-4}
p-F	10.5×10^{-4}	9.46×10^{-4}	9.42×10^{-4}
m-OH	4.64×10^{-3}	4.06×10^{-3}	3.47×10^{-3}
p-Cl	1.02×10^{-2}	9.17×10^{-3}	8.05×10^{-3}
p-CH_3	1.99×10^{-4}	2.05×10^{-4}	1.86×10^{-4}
H	1.18×10^{-3}	1.11×10^{-3}	1.03×10^{-3}
m-F	2.94×10^{-2}	2.79×10^{-2}	2.43×10^{-2}
p-NO_2	631.0		
m-NO_2	1.59		
m-Cl	4.85×10^{-3}	3.70×10^{-2}	3.72×10^{-2}

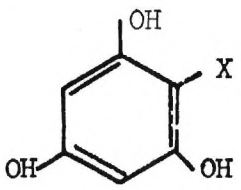
Figure II



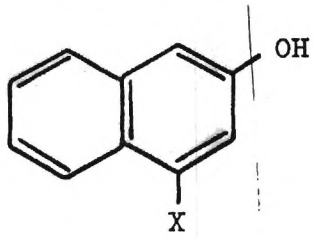
The results with the substituted fluorobenzenes indicate that the m-hydroxyl substituent shows no marked rate enhancement. Thus, one hydroxyl group on an aromatic ring does not provide enough driving force for ketonization. It is planned to investigate the effect of two and three hydroxyl groups by studying the rates of reaction of the following series of compounds with piperidine (A and B)



A



B



C

In addition, substitution of naphthol halides, C, should be of interest since β-napthols are known to have ketonic properties.

10. Neutron Diffraction and Mössbauer Effect Studies of Phase Transitions in Transition Metal Alloys - D. W. Forrester, S. Spooner

Research Goals: This research project is an effort to combine the techniques of neutron diffraction and the Mössbauer effect as a basis for systematic study of atomic order-disorder and magnetic phase transitions in transition metal alloys. The two techniques are being used to study transition metal binary alloys which are made up of neighbors in the periodic table and hence not readily susceptible to other experimental investigations. Among the alloys of this kind there are many commercially important materials, especially iron based alloys which are receiving primary attention in these studies.

Significant Results: A computer program has been written which calculates the Mössbauer absorption spectra structure for binary alloys as a function of short-range atomic order and concentration. This program has been used to generate the spectra to be anticipated in the alloys phases of Fe_3Co, FeCo, $FeCo_3$, FeNi, Ni_3Fe, FeCr, Fe_3Cr, Cr_3Fe and others. Data taken thus far on several of these alloys are in qualitative agreement but the data are extremely sensitive to heat treatment. Considerable effort has been made to produce heat treated samples which are powdered, homogeneous, and oxide free. A technique has been developed to achieve a quench in the order of a second.

The accurate description of the ordering phenomena in the iron-cobalt system has come into question in the past few years. On one hand a continuous series of CsCl-like ordering over a wide composition range has been assumed while an alternative description assumes the existence of several distinct ordered phases in the same composition range. In order to test the

validity of either assumption, a Fe-25%Co alloy was fabricated by arc melting, homogenized at 1000°C for several days and then ordered at 490°C for 200 hours. If a separate ordered structure is formed then diffraction lines should appear which make a positive identification of this phase. Neutron diffraction patterns before and after the ordering anneal indicate that a CsCl-like ordered phase appears and that no separate phase is present. This confirms earlier Russian and Japanese work but with the additional finding that the CsCl-like ordered can be detected at 25%Co composition.

11. Organic Reactions Induced by Electromagnetic Radiations - E. Grovenstein, Jr.

Research Goal: The research goal is aimed at study of the effect of various forms of radiant energy upon organic compounds, with the hope of discovering novel organic reactions, novel reaction mechanisms, and new reactive species.

Irradiation of Neophyllithium: The photochemistry of organoalkali compounds has been little studied. Photolysis of phenyllithium in ether has been reported by van Tamelen and co-workers[1] to give biphenyl in 80% yield. Also the photolysis of sodium cyclopentadienide in t-BuOh-tetrahydrofuran gave some 5% yield of two dimeric photoproducts, meso and dl-3-(3'-cyclopentenyl)-cyclopentenes[2]. Screttas[3] has briefly noted that photolysis of t-butyllithium gave LiH and lithium metal. Finally photolysis of phenyllithium (and related

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1 E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, J. Am. Chem. Soc., 87, 4964 (1965).

2 E. E. van Tamelen, et al., ibid. 89, 5073 (1967).

3 C. G. Screttas, Ph.D. Thesis, Univ. of Tenn., (1966).

compounds) in presence of polynuclear aromatic hydrocarbons such as anthracene has been reported to give the radical anion of the aromatic hydrocarbon and biphenyl.[4]

In the present work photolysis for 13.5 hours at -74° of a filtered solution of neophyllithium (2,2-dimethyl-2-phenylethyllithium) in tetrahydrofuran in a quartz apparatus with a mercury lamp gave after carbonation about the same (ca. 50/50) mixture of carboxylic acids (chiefly 3-methyl-3-phenylbutanoic acid) and hydrocarbons as an identical preparation of neophyllithium which had been subjected to the same conditions except for omission of irradiation. It is clear, therefore, that thermal decomposition of neophyllithium, even at this low temperature, exceeds photochemical decomposition. The chief contribution of this work has been develoment of a procedure for preparation of neophyllithium from neophylchloride in high yield (86%) in tetrahydrofuran solution.

Since it is well known that organoalkali compounds of alkali metals of higher atomic number than lithium differ remarkably in properties from organolithium compounds, the preparation and properties of neophylcesium (potassium) have been briefly investigated. This organoalkali reagent was prepared by reaction of neophylchloride in tetrahydrofuran with the eutictic alloy of cesium and potassium under the conditions given in Table I. Because of the very short life time of neophylcesium (potassium) in tetrahydrofuran, as revealed in this table, the photolysis of this organoalkali compound has not been undertaken. The most interesting result of the present work is that neophylcesium (potassium) rearranges in part to a 2-phenyl-2-butylcesium (potassium)

[4] H. Winkler et al., Chem. Comm., 3, 70 (1966) J. Org. Chem., 32, 1695 (1967).

with migration of a methyl group. Such migration of a methyl group in a simple hydrocarbon anion has not been previously reported; future work is planned to determine whether or not this rearrangement is an intramolecular process.

Irradiation in a Microwave Discharge: No more work upon irradiation of simple compounds with electrons in a microwave discharge has been carried out during the period of the present report.

Irradiation of Naphthalene and Related Compounds: A preliminary report of the work on "Photochemical Reactiions of Naphthalene with Dimethyl Acetylenedicarboxylate" has been completed (see Attachment I). This report after some revisions will soon be submitted for publication.

The photochemical cyclization of dimethyl α-naphthylmaleate to dimethyl trans-acenaphthene-1,8-dicarboxylate is being investigated in greater detail. So far this cyclization has proceeded in good yield in methyl alcohol and in dioxane containing 1% water but has proceeded in poor yield in anhydrous benzene. The solvent effect on the cyclization is being investigated further, particularly with respect to whether or not protons in the solvent participate in the photochemical process.

Publication of Work: The paper mentioned above will soon be ready for publication. No publications of the work have appeared during this period nor have any papers been presented at scientific meetings.

Table I

Reaction of Neophyl Chloride with Cesium-Potassium Alloy

	Run 1	Run 2
Neophyl chloride, mmols	16.7	16.1
Cesium, mg. atoms	41.9	36.1
Potassium, mg. atoms	39.1	33.2
Temperature, °C	-60°	-40°
Time of addition of neophyl chloride	8 min.	5 min.
Additional time before carbonation	30 min.	2 min.
Products of Carbonation:		
hydrocarbons, wt. %	58%	44%
volatile acids, wt. %	15%	24%
non-volatile acids, wt. %	27%	32%
Analysis of Volatile Acids by vpc:*		
unknown (retention time, 10.1 min.)	20%	23%
$CH_3CH_2CPh(CH_3)CO_2H$ (13.4 min.)	10%	8%
$PhC(CH_3)_2CH_2CO_2H$ (17.0 min.)	26%	47%
unknown (26.2 min.)	39%	18%

* Vapor phase chromatography of the methyl esters on diethylene glycol succinate column at 157°.

Attachment I

Photochemical Reactions of Naphthalene with Dimethyl Acetylenedicarboxylate

Erling Grovenstein and Thomas C. Campbell

(Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332)

While the photochemical reactions of benezene with olefinic and acetylenic derivatives have been studied in considerable detail and the mechanisms of these reactions are now partially understood,[1] corresponding reactions of naphthalene have been little investigated. No photochemical reaction of naphthalene with maleic anhydride has been found.[2] While the present work was in progress,[3] naphthalene was reported[4] to undergo a photochemical addition to diphenylacetylene to give an adduct of structure I; similar products were obtained from dimethylnaphthalenes. More recently naphthalene was reported to form two 1:1 photoadducts with cyclooctene; the structure of the major adduct was said to be consistent with structure II on

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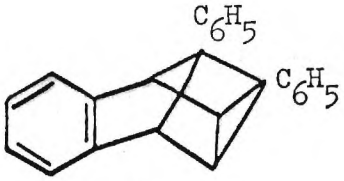
1 D. Bryce-Smith and H. C. Longuet-Higgins, Chem. Comm., 593 (1966) and references cited therein.

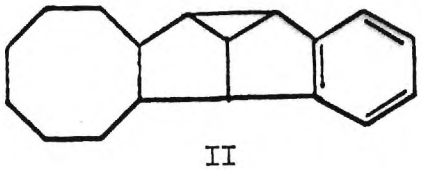
2 G. O. Schenck, J. Kuhls, S. Mansfield, and C. H. Krauch, Chem. Ber., 96 813 (1963).

3 We wish to thank Messrs. W. E. McGonigal, P. G. Arapakos, F. W. Walker, and J. Cone for conducting many of the difficult preliminary phases of this investigation.

4 W. H. F. Sasse, P. J. Collin, and G. Sugowdz, Tetrahedron Letters, 3373 (1965).



I



II

the basis of spectroscopic evidence.[5] We wish to report some new types of photochemical adducts from reaction of naphthalene with dimethyl acetylenedicarboxylate.

Irradiation of a solution of 0.16 mole of dimethylacetylenedicarboxylate in 2.4 moles of molten naphthalene at 90 ± 5° with ultraviolet light for four days in a quartz apparatus previously described[6] gave a complex mixture of products from which unreacted naphthalene was separated by distillation in vacuo at 100° and less soluble materials were removed by solvent precipitation from petroleum ether. The soluble product according to vapor phase chromatography (vpc) contained about an 11% yield of 1:1 adducts. These are designated, in order of increasing retention times, as III-VIII and were formed in relative proportions of 3, 34, 6, 34, 10, and 13% respectively. The more abundant products IV and VI were separated by liquid chromatography on silica gel and were purified by recrystallization from methanol and methylene chloride-

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5 D. Bryce-Smith, A. Gilbert, and B. H. Orger, Chem. Comm., 512 (1966).

6 E. Grovenstein, Jr., and S. P. Theophilou, J. Am. Chem. Soc., 77, 3795 (1955).

peteoleum ether respectively. Irradiation of a solution of 0.16 mole of dimethyl acetylenedicarboxylate and 0.47 mole of naphthalene in methanol at reflux temperature for 60 hours gave some 10% yield of 1:1 photoadducts IV, VI, VII, and VIII in relative amounts of 8, 7, 9, and 76% respectively. Following an isolation procedure like that for IV and VI, adduct VIII was obtained in 7% overall yield after recrystallization from methanol.

Adduct III, which was not formed in appreciable quantity in the photochemical reaction at lower temperature, was found to be identical in vpc retention time on two columns (Apiezon L and silicone gum rubber) with the 1:1 adduct formed by thermal reaction of dimethyl acetylenedicarboxylate with excess naphthalene (23% yield of crystalline adduct after 3 days at 170-180° in a sealed tube or 5.5% yield after 7 days at steam bath temperature). According to its mode of formation this adduct,[7] m.p. 76.5-77.0° from methanol, should have the structure of dimethyl 2,3-benzo-bicyclo [2.2.2]octatriene-5,6-dicarboxylate expected for a normal Diels-Alder addition. This structure was confirmed by hydrogenation to give a product of mp 90.5-91.0°, identical in melting point and nmr spectral comparisons with the reported values for exo-dimethyl 2,3-benzobicyclobicyclo[2.2.2]octane-5,6-dicarboxylate[8].

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[7] All crystalline adducts reported here had satisfactory C,H-analyses and molecular weight for $C_{16}H_{14}O_4$.

[8] K. Takeda, K. Kitahonoki, M. Sugiura, and Y. Takano, Chem. Ber., 95, 2344 (1962); K. Tori, Y. Takano, and K. Kitahonoki, ibid., 97, 2798 (1964).

Photolysis of thermal adduct III (0.01 mole) in methanol under a nitrogen atmosphere for 11 hours in the usual apparatus[6] but with a Pyrex filter gave 80% yield of a white crystalline product, mp 77.0-77.5°, which was identical in vpc retention time on two columns with the adduct V noted earlier. This compound[7] is assigned the structure of dimethyl 1,2-benzocyclooctatetraene 5,6-dicarboxylate on the basis of the following data: $\lambda_{max}^{C_2H_5OH}$ (mμ) 200(ε 30,500), shoulders at 230 (ε 20,500) and 270 (ε 1,800; nmr (CCl_4) at τ 2.9 (4 H, symmetrical multiplet), 3.29 (2 H, doublet, J 11 cps), 3.89 (2 H, doublet, J 11 cps), 6.35 (6 H, singlet); saponification gave an acid which readily yielded a cyclic anhydride, mp 196-197°, of satisfactory C,H-analysis for $C_{14}H_8O_3$[$\nu_{max}^{CCl_4}$ (μ) 5.42 (s) and 5.65 (s)]; hydrogenation over a palladium catalyst in ethyl acetate resulted in uptake of 3 molar equivalents of hydrogen. In addition to the cyclooctatetraene derivative V small amounts of two unidentified products were formed during the photolysis of III. This photolysis finds close analogy in the photolysis of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene to give tetrafluorobenzocyclooctatetraene as chief product in absence of a sensitizer.[9]

The pale yellow photoadduct IV, mp 62.0-63.0°, is assigned the structure of dimethyl 1-naphthylfumarate:[7] λ_{max}^{EtOH} (mμ) 223 (ε 63,000), 264 (shoulder, ε 4,400) 272 (ε 5,430), 281 (ε 5,780), 288 (shoulder, ε 4,760); nmr (CCl_4) at τ 2.2 to 3.0 (8 H, complex multiplet), 6.52 (3 H, singlet), 680 (3 H, singlet). Hydrogenation over a palladium catalyst resulted in uptake of 1 molar equivalent of hydrogen to give a white compound of

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[9] J. P. N. Brewer and H. Heaney, Chem. Comm., 811 (1967); cf. H. E. Zimmerman and G. L. Grunewald, J. Am. Chem. Soc. 88, 183 (1966).

mp 60.0-60.5° which was identical to a sample of dimethyl 1-naphthylsuccinate prepared from the known compound 1-naphthylmaleic anhydride.[10] Since the methyl ester of 1-naphthylmaleic acid was an oil of different vpc retention time from IV, the crystalline photoadduct IV is evidently the trans isomer, dimethyl 1-naphthylfumarate.

The colorless photoadduct VI, mp 86.7-87.0°, is provisionally assigned the structure 7 of dimethyl 3,4-benzotricyclo[3.3.0.$0^{2,8}$]octa-3,6-diene-6,7-dicarboxylate: λ_{max}^{EtOH} (mμ) 200 (ε 42,500), 220 (shoulder, ε 19,650), 265 (ε 4770); nmr (CCl_4) at τ 2.50 to 3.05 (4 H, complex multiplet), 5.87 (1 H, doublet, J = 5.9 cps), 6.42 (3 H, singlet) 6.45 (3 H, singlet), 6.53 to 6.86 (2 H, complex multiplet), 6.91 to 7.25 (1 H, complex multiplet). Hydrogenation with a palladium catalyst in glacial acetic acid resulted in the uptake of 2 molar equivalents of hydrogen. No deuterium exchange (nmr analysis) was observed after refluxing in 0.5 M $NaOCH_3$ in CH_3OD for 48 hr. Oxidation by $KMnO_4$ in aqueous acetone containing a little acetic acid and esterification of the acidic products with diazomethane gave 55% yield of dimethyl phthalate (vpc analysis) and small amounts of unknown compounds of longer retention times.

The photoadduct VII is formed in low yield and so far has resisted attempts at isolation in a pure state.

The colorless photoadduct VIII, mp 84.5-85.0° is assigned the structure[7] of dimethyl trans-acenaphthene-1,8-dicarboxylate: λ_{max}^{EtOH} (mμ) 226 (ε 84,800), 267 (ε 3840), 277 (ε 6480), 287 (ε 7690), 291 (ε 5690), 298 (ε 5150), 304 (ε 1790), 315 (ε 663), 319 (ε 431); nmr (CCl_4) at τ 2.34 to 2.86 (6 H,

[10] L. Denivelle and D. Razavi, Compt. Rend., 237, 570 (1953).

complex multiplet), 4.95 (2 H, singlet) 6.33 (6 H, singlet). The adduct failed to absorb hydrogen under general conditions which were successful with other adducts reported here. Saponification with alcoholic KOH gave the corresponding acid, mp 205-208° (dec), which with lead tetraacetate[11] in pyridine for 5 min. at 70° gave acenaphthylene (21% yield by vpc analysis or 8% yield by isolation of crystals, mp 90.0-91.0°) identified by comparison with a commercial sample. The more stable trans structure is assigned to VIII in view of failure to detect any appreciable isomerism of VIII with sodium methoxide in CH_3OD under conditions which exchanged the hydrogen atoms alpha to the carbomethoxy groups, failure to obtain a volatile anhydride (vpc analysis) upon refluxing the acid with acetic anhydride, and failure of the corresponding di-N-benzylamide to give a cyclic imide in trifluoroacetic acid under conditions wherein the di-N-benzylamide of naphthalene-2,3-dicarboxylic acid gave an imide in good yield.

While photoadducts VI and VIII appear to be stable under conditions of irradiation with uv light, dimethyl 1-naphthylfumarate (2.9 mmoles) in methanol solution upon irradiation in the usual apparatus (but with a Pyrex filter) for 11 hours, under nitrogen atmosphere at room temperature, gave 59% yield of dimethyl trans-acenaphthene-1,8-dicarboxylate (VIII). Irradiation of dimethyl 1-naphthylmaleate under similar conditions also gave dimethyl trans-1,8-dicarboxylate in a yield of greater than 74%.[12]

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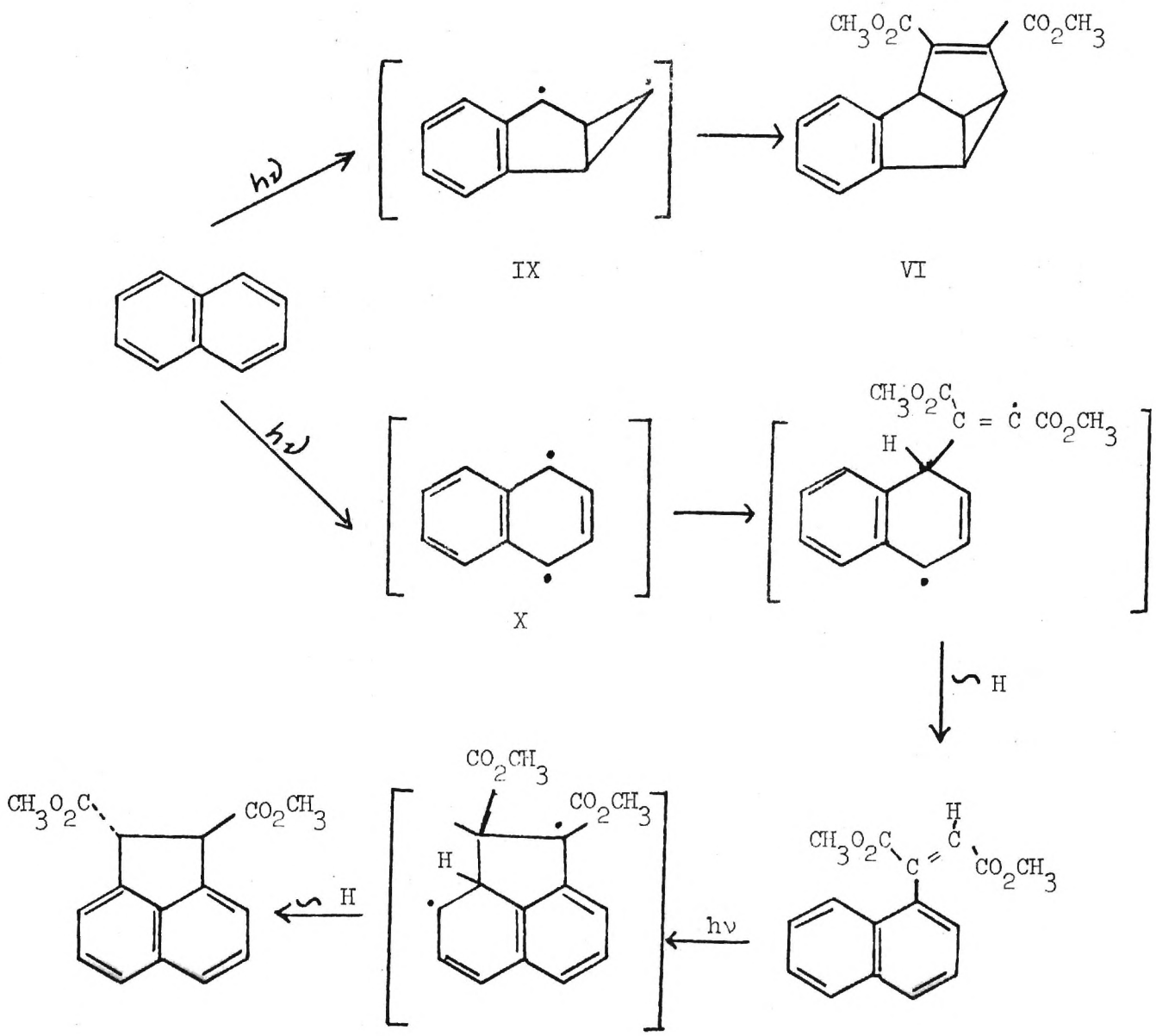
[11] E. Grovenstein, Jr., D. V. Rao, and J. W. Taylor, J. Am. Chem. Soc., 83, 1705 (1961).

[12] We are indebted to Mr. Tomoo Shibata for this result.

Since the same 1:1 adducts (though in reduced yield) are obtained on reaction of dimethyl acetylenedicarboxylate with molten naphthalene with use of Pyrex filter as without a filter, the present photochemical reactions likely are initiated by photoexcitation of naphthalene which then combines with the acetylenic ester. The photoadducts, IV, VI, and VIII are conveniently rationalized by the scheme shown below.



Intermediates IX and X are presumed to be in singlet and triplet states respectively in analogy with corresponding biradicals from photoexcitation of benzene.[1] The formation of VI is similar to the photoreaction of naphthalene with cyclooctene to give II.[5] The photocyclization of IV to VIII is somewhat similar to the photochemical transformation of trans- 1,3-diphenylpropene to 1-phenylindane (among other products)[13] and the photocyclization of alkyl-substituted acrylic acid anilides to dihydrocarbostyrils.[14]

Acknowledgment: Support by the U.S. Army Research Office (Durham) under Grant No. DA-ARO(D)-31-124-G258 and the National Aeronautics and Space Administration Grant NsG-657 is gratefully acknowledged.

12. Large Dynamic Deflections of Shallow Arches and Shells Under Aperiodic Loads - W. W. King

Analytical study of dynamic snap-buckling of shallow shell-like structures has been continued. Equations of motion have been developed to describe nonlinear interaction of symmetric and asymmetric motions of a shallow circular arch using both Marguerre and Donnell representations. Ordinary differential equations, generated by application of the Galerkin method to the partial differential equations of motion, have been programmed for analog computation for the case of a finite-duration pulse load.

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[13] G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, J. Am. Chem. Soc., 87, 1410 (1965).

[14] P. G. Cleveland and O. L. Chapman, Chem. Comm., 1064 (1967).

13. An Investigation of the Strengthening Mechanisms Involved in Precipitation Hardened and Dispersed-Phase-Strengthened Alloys - E. A. Starke, Jr.

Small-angle x-ray scattering techniques and hardness measurements have been used to study pre-precipitation in two-Al-Zn-Mg alloys containing the same Zn content (2.46 at. %) but different Mg contents. The following conclusions have been reached:

(a) Changes in the zone size follow the same pattern as the changes in hardness so that a close correlation appears to exist between the strength of these alloys and the size of the zones.

(b) A critical zone size is required for the nucleation of the intermediate precipitate. The critical zone size appears to be dependent on the alloy composition. In the present study it was found to be approximately 43 A for the 0.72 at. % Mg alloy and approximately 33 A for the 1.09 at. % mg alloy.

(c) The role of Mg as a reversible-vacancy trap has been established. It has also been shown that Mg governs the concentration of Zn in the zones.

(d) Higher Mg content induces a greater extent of quench clustering, resulting in a large as-quenched hardness difference in alloys having only slightly different Mg contents.

Some of the results of this work were presented in a talk entitled "Structure-Property Correlations During Ageing of Two Al-Zn-Mg Alloys" at the 1967 Fall Meeting of the Metallurgical Society of the AIME.

This work has produced a technical paper entitled "Pre-Precipitation in Al-Zn-Mg Alloys Studied by Hardness and Small-Angle X-ray Scattering

Measurements" which has been accepted for publication in the Journal of Material Science.

This research should lead to a better understanding of the ageing characteristics of the commercial Al-Zn-Mg alloys such as 7075.

14. A Study of Inflatable Shells - C.E.S. Ueng

Based upon the finite-deflection theory, which is necessary for such a problem, the governing equations and the boundary conditions were first obtained through a variational approach. This set of equations, as well as the boundary conditions, is quite general and complicated. The strong nonlinearities involved prohibit any solutions with a reasonable amount of effort. From a study of the order of magnitude, as usually adopted in the development of shell theories, certain less important nonlinear terms were, therefore, dropped. The attention was then focused on the use of the equations and boundary conditions to solve a simple problem, namely, a finite circular cylindrical inflatable shell subject to a ring load at the center. The results indicate that the stresses induced by inflation and by external loading tend to counteract each other, thus the inflatable shell is safe if external loads and inflation are applied simultaneously, but unsafe with respect to inflation alone. This is quite different from conventional structures. This portion of the results is being written up and is to be submitted to a related technical journal.

The following problems were discovered during the course of this research and are either unfinished or not started yet:

(1) The investigator has not found out the reason why the inconsistent frequency of the lowest mode of an inflatable plate

obtained in references 1 and 2 exists.[1,2]

(2) The stability problem of inflatable shells: In recent years it has been studied and concluded that the problem of elastic stability of a rod under tension does exist. It has also been noted that an inflatable spherical balloon subject to internal pressure can lose its stability for a critical pressure. This may have significant importance in the application of this type of structure in space exploration.

(3) In connection with the results obtained and reported earlier, and Problem 2 mentioned above, it is obvious that there is a need to study the deployment problem where time must be brought in as an independent variable.

15. Microwave Absorption by Gases - T. L. Weatherly, J. Q. Williams

The microwave absorptions studied are associated primarily with changes in molecular rotation energies. However, the absorption frequencies are influenced slightly by nuclear electric quadrupole moments and, in the case of an applied electric field, by the molecular dipole moment. The purpose of these studies is to test the theory for quadrupole interactions in molecules containing two and three identical quadrupolar nuclei and to measure the quadrupole coupling constants and electric dipole moments of such molecules.

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[1] H. G. McComb, "A linear theory for inflatable plates of arbitrary shape," NASA TN D-930, October 1961.

[2] F. H. Ho and W. A. Nash, "Nonlinear free transverse vibrations of inflatable shallow shells," Proceedings of the 5th National Congress of Applied Mechanics, Minneapolis, Minnesota, June 1966, p. 127.

The work on second order effects in molecules containing two identical nuclei is progressing, but it is not yet possible to draw definite conclusions. The measurements on the Stark effect of the J = 2 - 3 transitions in $CHCl_3$ and $CFCl_3$ are almost complete, and the results will be given in the next report.

Publications: "Hyperfine Structure in the Microwave Spectra of $CFCl_3$ and $CHCl_3$," A. A. Wolf, Quitman Williams and T. L. Weatherly, J. Chem. Phys. 47, 5101 (1967).

"Quadrupole Hyperfine Structure in the Microwave Spectra of Phosphorous Trichloride and Phosphoryl Chloride," C. R. Nave, T. L. Weatherly and Quitman Williams, accepted for publication in the Journal of Chemical Physics.

16. The Significance of K-Ar Ratios in Fine-Grained and Glassy Materials - C. E. Weaver, J. M. Wampler

The objective was to determine the relative diffusion rates of K and radiogenic Ar in fine grained materials under a variety of environmental conditions.

Biotite samples were leached with a variety of solutions for varying lengths of time to determine the rates at which K and Ar are removed. X-ray analyses were made showing how the degree of interlayer expansion or hydration (weathering) varied as a function of K removal. K and Ar analyses of these samples are in progress. The K-Ar age of a naturally weathered soil biolite was essentially the same as that of the underlying fresh biotite.

Considerable time has been spent modifying the mass spectrometer to improve resolution in the argon mass range. The sample fusion and gas purification system has been partly rebuilt to reduce the level of atmospheric argon and other contaminants. Both precision and accuracy has been greatly

improved.

Mössbauer analyses of iron in clay minerals continued. The Mössbauer technique was used to determine the extent of oxidation of Fe during weathering of biotites. It was also shown that as the amount of fixed K in expanded clays increased the Fe^{3+}/Fe^{2+} ratio decreased. The reduction of the Fe apparently increased the layer charge and allowed for an increase in the amount of K-fixation and layer contraction.

17. Investigation of the Theory of Plastic Waves -

E. R. Wood

The rate-independent plastic wave solution for a fixed-free bar, mentioned in the last report, was written up as a Master's Degree special project.

The analysis for determining the dynamic plastic response of a finite bar, including strain-rate effects, was completed. A computer program was then developed for the UNIVAC 1108 computer, which provides the stress-strain time history of the bar at all stations along its length for a time equivalent to its natural undamped period.

Results of this analysis indicated that it would be desirable if one could determine the stress-strain time history of the bar for a considerably greater period of time. The computer program was then extended to provide results for periods of time up to twelve times the natural period of the bar.

An important feature of the analysis is that it makes use of a bilinear representation of the stress-strain curve where the slope of the plastic region of the curve can be varied. This permits studies of dynamic plasticity for materials ranging all the way from elastic to perfectly plastic. Studies have recently been made on the computer of the effects of this variation

on the resulting dynamic plastic response of the bar.

B. TRANSPORT PHENOMENA

1. Combustion and Flame Propagation Under Applied Electric Fields - P. Durbetaki

The initial objectives of this analytical and experimental project were to study the electrostatically augmented ion movement effects on (a) the improvement of ignition characteristics of a main stream combustible mixture and (b) the reaction propagation in a flow field over a surface. Preliminary analysis and lack of continuity in support of this project resulted in a reevaluation of the problem. The research activity was then shifted to another area, still within the broad objectives of the title. This area is concerned with the two-phase solid-gas reactive flow phenomena, which are important in many energy conversion and propulsion devices. The research activity, part of which was carried out with NASA support, is aimed at an analytical and experimental study of (1) particle injection into the boundary layer of a reactive flow system through a slot at a wall; (2) movement and distribution of the particles in the boundary layer and the main stream; (3) ignition of the particles and flame propagation with and without the presence of a static electric field.

The first part of the work considered the problem of laminar flow of a viscous gas over a semi-infinite flat plate with wall-slot injection of solid particles. The analysis treated the particles as a continuum. A continuity equation, two conservation of momentum equations and an energy equation were used to represent the particle flow. These equations together with the continuity, momentum and energy equations for the gas phase and the appropriate boundary conditions described the problem mathematically.

The coupling of the momentum equations by the shear between the two phases resulted in the necessity of solving simultaneous partial differential equations. The finite difference technique was employed to handle this difficulty.

The injection velocity and angle were varied to study various flow situations. Flow situations with parallel component of the injection velocity both less than and greater than the free-stream velocity were investigated yielding velocities and densities necessary to describe the flow of the two phases. The temperature profiles were obtained through similarity considerations.

An examination of the results indicate a thickening of velocity profiles in all cases analysed. Also the fluid x-velocity and the particle x-velocity approach each other as the flow proceeds downstream. For greater than free-stream x-injection velocities the profiles maintain a maximum within the boundary layer. The maximum of both the fluid and x-velocities occur at approximately the same distance above the plate. The particle density profiles indicate that once the flow has moved downstream all profiles appear to achieve a similar form. The density is zero at the plate and at the edge of the particle boundary layer reaching a maximum at some midpoint. The particles disperse as the flow proceeds downstream reducing the particle density to values which are considerably less than the injection density.

2. A Boundary Value Problem for Quadratic Differential Equations with Applications to Boundary Layer Theory - D. V. Ho, H. K. Wilson

As reported previously, the purpose of this study has been to investigate the existence and uniqueness questions for the solution of the boundary value problem

$$y''' + yy'' + \lambda(h - y'^2) = 0,$$

$$h'' + yh' = 0,$$

$$y(0) = y'(0) = 0,\ h(0) = a,\ y'(\infty) = h(\infty) = 1,$$

which governs the similarity solution for a compressible boundary layer flow with non-zero pressure gradient over a cold wall ($a \leq 1$).

The existence part of the study has been completed, and a paper by the investigators, under the title "On the Existence of a Similarity Solution for a Compressible Boundary Layer", was subsequently published in the Archive for Rational Mechanics and Analysis, vol. 27, no. 2, p. 165-174, in December, 1967.

Little progress has been made in the study of the uniqueness question. The investigators fully realize and appreciate the challenge of this problem. It is hopeful however that given time, a uniqueness theorem can be produced.

As a consequence of the investigators' studies, J. Serrin at the University of Minnesota and J. B. McLeod in England have written two papers, one entitled "The behavior of similar solutions in a compressible boundary layer" to appear in the Journal of Fluid Mechanics, and the other "On the existence of similar solutions for some boundary layer problems" to be published. The former discusses how similarity solutions, if they exist, must behave and their physical meanings, based in part on the investigators' results. The latter extends the investigators' existence theorem to cover the case of a heated wall ($a \geq 1$) as well as the convection problem studied by the investigators under this grant in the summer of 1965.

3. Ion Energy Loss in Thin Films - J. W. Hooper

Prior to the initiation of the subject period, this project received external financial support from the U. S. Atomic Energy Commission as part of project A-668 as covered by Modification No. 5 of Contract No. AT-(40-1)-3027. Residual funds remaining in NASA Project B-705 were therefore returned to the Space Sciences and Technology Board for distribution as required by other projects. It should be noted here that NASA support was instrumental in leading to AEC project funding. Such support is gratefully acknowledged.

As noted above no work under the auspices of NASA was conducted during the period covered by this report; however in the interest of completeness the following project description is provided.

The objective of this research is the determination of the integral energy loss experienced by protons and singly charged lithium ions upon passage through thin films of aluminum, gold, and carbon. The use of ion beam energies in the range 2 keV to 20 keV is expected to develop useful application results as well as provide meaningful checks of existing theoretical treatments. Efforts have been directed toward the determination of the most feasible program of study and toward the development of the facilities required for such studies. The following experimental program phases have been selected:

(a) The energy distribution of Li^+ and H^+ ions passing through thin films of C, Al_2O_3, and Au at very small scattering angles will be determined.

(b) Total numbers of emergent particles, and where possible the charge states of such particles, at very small scattering angles will be evaluated.

(c) The distribution of energies (velocities) of particles emerging from the thin films at various angles will be determined.

(d) Total numbers of emergent particles and where possible the charge states of such particles will be determined for various emergence angles.

An ultrahigh vacuum vacion type pumping system together with associated controls has been developed for use with this experiment. The design for the energy analysis of the particles of part (a) above has been completed together with a solid state detector calibration system. A 10 KV power supply has been purchased and the necessary solid state detector and carbon films are on hand. Phase (a) of the experimental program is now in progress.

4. Transition and Slip Flow - A. B. Huang

A brief description of the present status of the research program supported by NASA Multidisciplinary Research Grant NsG-657 is included. In this program several non-linear re-entry problems in gas dynamics have been solved from the molecular approach of kinetic theory using the Boltzmann equation as the fundamental governing relation and using the discrete ordinate method as a tool. The method as applied to the solution of both steady and unsteady non-linear B-G-K Boltzmann equation has been established on a rigorous, fundamental, and systematic basis. The results obtained in this study represent, to the best of the author's knowledge, the first meaningful solution to the nonlinear and two-dimensional B-G-K Boltzmann equation. It is thus concluded that the proposed method is a powerful tool for solution of some practical rarefied gasdynamic problems.

Publications: A. B. Huang, "Slip Coefficient of a Gas," Physics of Fluids, 11, 61-63, (1968).

A. B. Huang, "Kinetic Theory of the Transient Couette Flow Problem," Physics of Fluids, 11, 446-448, (1968).

A. B. Huang and D. L. Hartley, "Nonlinear Rarefied Couette Flow with Heat Transfer," Physics of Fluids, 11, 1321-1327 (1968).

A. B. Huang and D. L. Hartley, "Nonlinear Rarefied Rayleigh's Problem," AIAA J., (accepted for publication).

A. B. Huang and D. L. Hartley, "Kinetic Theory of the Sharp Leading Edge Problem, Supersonic Flow," Physics of Fluids (to be published).

A. B. Huang, "Kinetic Theory of the Rarefied Supersonic Flow over a Finite Plate," Proceedings of the 6th International Symposium on Rarefied Gas Dynamics, MIT, Boston, July 22-26, (1968).

A. B. Huang and P. F. Hwang, "Kinetic Theory of the Sharp Leading Edge Flow, Hypersonic Flow," to be presented at the 19th International Astronautical Congress, New York, Oct. 13-19 (1968).

Utilization of the Author's Method by Other Researchers: The discrete ordinate method established by the author for solving both linear and nonlinear Boltzmann equation has been widely utilized by other researchers in the field of rarefied gas dynamics. The following publications are some of them:

K. C. Reddy, "Rarefied Gas Flow in the Knudsen Layer," Physics of Fluids, 11, 1308-1311 (1968).

K. C. Reddy and D. C. Todd, "Nonlinear Knudsen Layer Flow," Proceedings of the 6th International Symposium on Rarefied Gas Dynamics, MIT, Boston, July 22-26 (1968).

5. Free Molecular Flow - G. A. Miller

Mr. Buice has continued his work on free-molecular flow through capillaries. There are no new results to report at this time. Mr. Buice is working toward the Ph.D., and his work will be described in detail in his thesis at a later date.

Mr. Siberts received an M.S. degree in June, 1968 for work done earlier on the project. The title of his thesis is "An Investigation of Thermal Transpiration in Porous Media."

6. Nonlinear Acoustics - G. M. Rentzepis

Scope: Nonlinear acoustical phenomena are characterized by finite amplitude sound waves, irreversible thermodynamic processes, energy jumps and their interactions. The concern of this project is the description of such disturbances, their motion, and the subsequent degeneration to sound waves and/or sound wave generators.

Final Report: The governing equations for this problem were introduced by making use of the fundamental equations of gas dynamics and the proper thermodynamic relationships. The resulting equations are sets of nonlinear differential equations. Known techniques of analysis for nonlinear differential operators were employed in an attempt to obtain meaningful solutions to this problem. Essentially solutions to two specific problems were sought: (i) The axisymmetric flow field was considered. In this case transformations were constructed by which the time dependent terms were made constant, thus rendering the problem to the possibilities of generating self-similar solutions associated with the axisymmetric flow problem. A finite difference scheme was constructed for numerical solutions to the flow field without discontinuities. (ii) The case of self-excited finite amplitude waves in ducts filled with a nonlinear viscous fluid. In this problem

perturbation procedures are employed seeking periodic solutions.

7. Studies of Finite Amplitude Phonons in Solids -

A. L. Stanford, W. E. Moody

During the reporting period, techniques were established to measure amplitudes of transverse waves in solids, a method that complements previous work using longitudinal waves.

Publications: Accepted for publication in Journal of the American Ceramic Society: J. Archer, W. E. Moody, and A. L. Stanford, Jr., "Third Oder Elastic Constant C_{111} in LiF."

8. Low Energy Ion Accelerator - E. W. Thomas

Objective: The principle objective of the work was the construction of a low energy ion accelerator which is to be used as the projectile source for a series of atomic collision experiments.

Results: The initial objective of constructing and bringing into operation a low energy ion accelerator has been accomplished. Beam currents of mass analyzed ions range up to 400μA. Protons and ions of atmospheric gases have been accelerated.

The first experiments to be carried out using this accelerator are now in the design stage. Study of ion implantation into semiconductor materials will be performed on behalf of a group in the Engineering Experiment Station. (Also funded by NASA but under an unrelated program). A sophisticated atomic scattering experiment is under construction. This is designed to study the interaction of atomic systems at small known interatomics separation.

In summary, the basic objectives of the construction of an ion accelerator have been achieved, and experiments are being constructed

which will utilize the facility.

9. Steady Three-Dimensional Viscous Flows Over Surfaces Possessing Geometric Singularities - J. C. Wu

The purpose of this research was to correlate results of unsteady flow problems of the Rayleigh flow type to three-dimensional problems and to extend existing numerical methods for two-dimensional boundary layer problems to three-dimensional problems involving surface geometric singularity. Three internal reports were prepared and dealt with, respectively, new results of Rayleigh's problem in two spatial coordinates and comparison of various solutions obtained from unsteady flow analogy to corresponding three-dimensional steady flow problems, comparisons of various existing numerical methods for the solution of boundary layer problems, and practical aspects of an explicit finite difference method for the solution of complex boundary layer problems. The differential equations and boundary conditions for corner and edge flow problems were established in a form suitable for numerical solution. A paper entitled "Generalized Rayleigh's Problem in Viscous Flows" was published in the Quarterly Journal of Mechanics and Applied Mathematics. A second paper entitled "Uni-directional Flow Along Corners and Edges" is being prepared for journal publication.

10. A Theoretical Investigation of Nonlinear Combustion Instability in Rocket Engines - B. T. Zinn

In the first phase of this investigation a simplified system of coupled nonlinear partial differential equations, capable of describing

"Generalized Rayleigh's Problem in Viscous Flows", J. C. Wu and T. Y. Wu, Quart. J. Mech. and Applied Math., XX-4, November 1967.

the nonsteady flow field in liquid-propellant rocket motors, was derived. Obtaining solutions to these equations was the objective of the second phase of this study.

Since most of the available nonlinear theories are very complicated and hence are not being used in practical applications, it was decided to look for a new solution technique that will enable the propulsion engineer to perform a nonlinear (as well as a linear) stability analysis with relative ease. A review and study of stability analyses performed in other branches of science and engineering revealed that the Galerkin method had the best potential of becoming a popular analytical tool that will be extensively used in the analysis of combustion instability problems. To reach this end the mathematical approach used in the classical Galerkin method had been modified to be applicable in the solution of combustion instability problems. The applicability of the modified approach was tested by using the method in the solution of a combustion instability problem whose solution was obtained with another method. The Galerkin method produced results that were in exact agreement with the available solution.

Publications: "Application of the Galerkin Method in the Analysis of Combustion Instability Problems."

This paper has been accepted for presentation at the 19th International Astronautical Congress to be held in October 1968 in New York. The paper is expected to appear in the proceedings of this conference.

In addition this work was invited for presentation at the 5th ICRPG Combustion Conference to be held in October 1968 in Silver Spring, Maryland.

This work will also be described in a seminar to be presented, by the principal investigator, on July 7, 1968 at the Technion (Israel's

Institute of Technology).

It is expected that the method developed in this study will become popular with those whose concern is the development of stable rocket engines.

C. SYSTEMS RESEARCH

1. Allocations Procedures for System Reliability Requirements - W. W. Hines

Description of Research: This research was initiated in the summer quarter of 1967. The research objectives related to the consolidation and extension of reliability allocation methodology with emphasis on the development of realistic, useful procedures for first level and second level system reliability allocation.

Publications: Fyffe, Hines, Lee, "System Reliability Allocation and a Computational Algorithm", IEEE Transactions on Reliability, Vol. R-17, No. 2, June 1968, pp. 64-70.

Submitted for publication : "Functional Allocation of System Reliability."

D. NUCLEAR PROCESSES

1. Neutron Reaction Cross Sections of Astrophysical Interest - R. W. Fink

A description of this research problem and its astrophysical significance is given in the previous Annual Report and Renewal Proposal (August and September, 1967). Measurements of neutron activation cross sections are in progress in the thermal (0.025 eV), 30-100 keV, and 14-15 MeV energy regions. What follows below is a brief summary of the results so far obtained and of current work in progress.

Neutron Cross Section Measurements on Kr and Xe Isotopes:

Owing to the difficulty of preparing suitable targets of the rare gases, there are essentially no data on neutron cross sections of any kind for Kr and Xe, except a few measurements at thermal energy, and these are very incomplete. Both elements are produced in high yield in fission, and a knowledge of their cross sections for neutron reactions is important for reactor design, particularly for fast reactors (suitable for propulsion or space applications). In addition, both elements are located at crucial places in the periodic chart of nuclides with respect to unraveling the slow neutron capture (s-process) and rapid neutron capture (r-process) of nucleosynthesis in stars and supernovae. The neutron capture, (n, γ), cross sections of the various isotopes of Kr and Xe are especially crucial in the keV energy region (25 - 100 keV) for this astrophysical interpretation, as discussed in the previous Annual Report (1967).

In order to perform such measurements on Kr and Xe, an interesting solid powdered target material* (rare gas quinol clathrate) of Kr and

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* Obtained commercially from Thorn Electronics, Ltd., Hook Rise South, Tolworth, Surbiton, Surrey, England. This material is composed of quinol rare gas clathrate, which is a compound of hydroquinone in which an atom of rare gas, such as Ar, Kr, or Xe is physically trapped in the crystalline cage of the compound. These rare gas quinol clathrate compounds are formed by crystallization of quinol solutions under high pressure (40 atmos) of rare gas, and they contain up to 9% by weight of Ar, 18% of Kr, and 26% of Xe, respectively. The approximate general formular is 3 quinol·X, where X is a rare gas atom and quinol is $C_6H_4(OH)_2$. The powder is stable at room temperature and can be kept for years with negligible gas loss. On dissolving the crystals in water, or on heating, the gas is released quantitatively and can be measured accurately by micro gas analysis.

Xe has been utilized for the first time by us for investigation of activation cross sections with thermal (0.025 eV), keV, and 14.4 MeV neutrons.

The quinol rare gas clathrate is very suitable for neutron irradiations, because no interfering activities are produced from the carbon, hydrogen, or oxygen.

Thermal Neutron Cross Section of Kr and Xe: The Kr-clathrate compound has been irradiated in the thermal neutron beam of the Georgia Tech reactor, with and without Cd wrapping (to take into account the small contribution due to the fast neutron component). The experiments on Kr-clathrate are completed, and the thermal cross sections are being calculated for the following observed reactions (using Ge(Li) detectors):

$Kr^{86}(n, \gamma)Kr^{87}$ (76 min)

$Kr^{84}(n, \gamma)Kr^{85m}$(4.4 h)

$Kr^{82}(n, \gamma)Kr^{83m}$(1.86 h)

$Kr^{80}(n, \gamma)Kr^{81m}$(13 sec)

$Kr^{78}(n, \gamma)Kr^{79}$ (34 h)

In these experiments, no prominent gammas were detected which could be attributed to possible thermal (n, α) reactions on Kr isotopes.

(E. Kondaiah and N. RanaKumar)

A similar set of measurements of the thermal neutron cross sections on the Xe-clathrate compound is currently in progress.

KeV Neutron Cross Sections of Kr and Xe: The (n, γ) cross sections of Kr and Xe isotopes are being measured with the quinol clathrate compounds, by using the Oak Ridge National Laboratory Van de Graaff accelerator, in a collaboration with Drs. J. H. Gibbons and R. L. Macklin. The neutron source, based on the $Li^{7}(p, n)$ reaction, provides monoenergetic

neutrons in the energy region from 30 to about 100 keV. Owing to the fact that the neutron output from the Van de Graaff is only about 10^6 neutrons/sec at 30 keV and to the fact that the cross sections are expected to be in the region of 10 to 100 mb, it is necessary to use large samples (5 to 15 grams). In such large samples, the question arises as to whether significant thermalization occurs. Our calculations show that our conical samples of 4 cm maximum height containing up to 12 grams of clathrate compound will give rise to fewer than 2 neutron collisions on the average for 30 keV neutrons (i.e., the calculated mean free path of a 30 keV neutron in clathrate is $\geq$ 2.5 cm), whereas the number of collisions required to thermalize a 30 keV neutron is about 28, on the basis of the carbon, hydrogen, oxygen composition of the clathrate.

This work is in progress to measure the following keV neutron activation cross sections, using a 10cc Ge(Li) detector with approximately 4 keV FWHM resolution at 1332 keV:

$Kr^{86}(n, \gamma)Kr^{87}$ (76 min)	[Pure r-process nucleus: Kr^{86}]
$Kr^{84}(n, \gamma)Kr^{85m}$ (4.4 h)	[Mixed r- and s-process nucleus: Kr^{84}]
$Xe^{136}(n, \gamma)Xe^{137}$ (4 min)	[Pure r-process and N = 82 closed shell nucleus: Xe^{136}]
$Xe^{134}(n, \gamma)Xe^{135m}$ (15.6 min)	[Pure r-process nucleus: Xe^{134}]
$Xe^{134}(n, \gamma)Xe^{135g}$ (9.2 h)	[Pure r-process nucleus: Xe^{134}]
$Xe^{132}(n, \gamma)Xe^{133m}$ (2.26 d)	[Mixed r- and s-process nucleus: Xe^{132}]
$Xe^{132}(n, \gamma)Xe^{133g}$ (5.27 d)	[Mixed r- and s-process nucleus: Xe^{132}]

(E. Kondaiah, N. RanaKumar, J. H. Gibbons, and L. Macklin)

Neutron Reaction Cross Sections of Kr and Xe at 14.4 $\pm$ 0.3 MeV: The (n, 2n), (n, p), and (n, α) reaction cross sections of Kr isotopes have been measured with the clathrate compound at 14.4 $\pm$ 0.3 MeV. The results are to be presented at the Am. Phys. Soc. meeting, Washington, D.C. (April 22-25, 1968), and the abstract is attached to this report.

Similarly, the 14.4 MeV neutron cross sections of Xe isotopes, using the Xe-clathrate compound are in progress.

The cross sections are all measured with an accuracy of 10% or better, on the improved mixed powder method of Rao and Fink, described below.

(E. Kondaiah and N. RanaKumar)

Other Cross Section Studies at 14.4 $\pm$ 0.3 MeV Neutron Energy: The (n, 2n), (n, p), and (n, α) activation cross sections of Si, Zn, Br, Rb, Se, and Fe have been completed and a copy of the abstracts for the Washington, D. C. meeting (1968) of the Am. Phys. Soc. are attached, together with reprints of papers published. The results are embodied in these abstracts and reprints.

Improved Accuracy in Neutron Cross Section Measurements by the Mixed Powder Method: The need for measuring activation cross sections to an accuracy of 10% or better is emphasized in a recent survey.[1] The controversy over the interpretation that some of the general trends in (n, 2n), (n, p), and (n, α) cross sections at 14 - 15 MeV are due to shell structure effects depends on the availability of accurate cross section values.

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[1] R. W. Fink, "Measurements by Improved Methods of Activation Cross Sections for 14.4 MeV Neutron Reactions," Proc. Conf. on Small Accelerators, Oak Ridge, Tenn. (Apr. 8-10, 1968) (Invited review paper); Preprint, U.S. AEC Report ORO-3346-18.

The mixture method of Rao and Fink[2], which takes advantage of the high resolution of Ge(Li) detectors, has the unusual advantage of measuring cross sections to such an accuracy using natural targets. The consistency and reliability of the method is demonstrated by the fact that the mean deviation in all values obtained for the $Al^{27}(n, \alpha)Na^{24}$ reaction cross section at 14.4 $\pm$ 0.3 MeV, under a variety of experimental conditions in the hands of various investigators over a two-year period, falls within the error limit (6%) of the primary standard reaction, $Fe^{56}(n, p)Mn^{56}$ (100 $\pm$ 6 millibarns). The $Al^{27}(n, \alpha)Na^{24}$ cross section is 113 $\pm$ 6 mb from 23 such measurements, in agreement with a large number of precision determinations using other techniques, as reported in the literature.

The mixed powder method was also employed successfully to standardize the cross section of the $Si^{28}(n, p)Al^{28}$ reaction, as discussed below, which is useful as a monitor for short-lived activities.

All cross sections presented in this report are based on the mixed powder method and Ge(Li) detectors. The extension of the method to measure cross sections at thermal and keV neutron energies represents a significant contribution to astrophysical cross section measurements.

(P. Venugopala Rao and R. W. Find)

Standardization of the $Si^{28}(n, p)Al^{28}$ Cross Section at 14.4 MeV and Its Astrophysical Application: The $Si^{28}(n, p)Al^{28}$ (2.3 min) reaction cross section was standardized to be 252 $\pm$ 15 mb at 14.4 $\pm$ 0.3 MeV against the $Fe^{56}(n, p)Mn^{56}$, $Al^{27}(n, \alpha)Na^{24}$, and $Al^{27}(n, p)Mg^{27}$ reactions, by using the mixed powder method.[2] The standardization was very

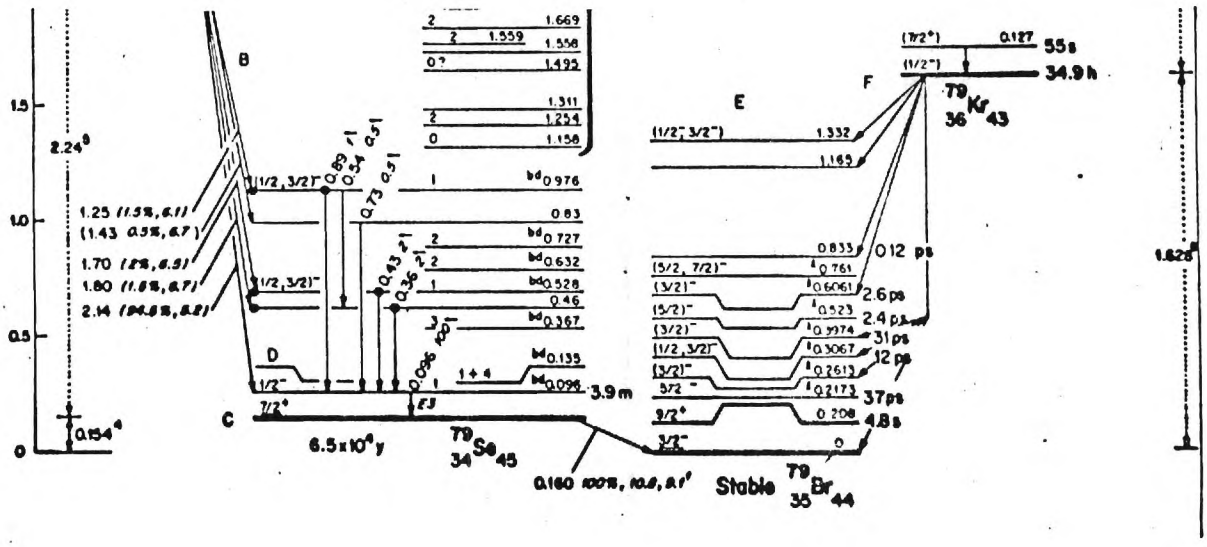
[2] P. Venugopala Rao and R. W. Fink, Phys. Rev. 154, 1023 (1967).

carefully performed, in order to make the reaction useful as a primary standard in the short half-life region, so that elemental silicon powder can be used in the rabbit samples as a monitor. This reaction has many attributes which make it an ideal monitor; e.g., the 2.3 min Al^{28} product has a simple decay scheme with 100% of the decays giving the high energy 1780 keV gamma, which has negligible internal conversion and self-absorption corrections, and the reaction has a large cross section giving a strong yield of activity. Finally, elemental silicon can be obtained in powdered form of zone-refined semiconductor grade purity and exhibits no spurious activities from impurities.

This reaction is of astrophysical application, since lunar, planetary, and terrestrial probes containing sealed 14 MeV neutron generators are being used for activation analysis in situ. The $Si^{28}(n, p)Al^{28}$ reaction will be one of the principal ones induced in 14 MeV neutron irradiation of such samples and can serve as a standard for determining the relative abundance of other elements by the activation method, especially if high resolution gamma spectrometry is included.

(N. RanaKuma and E. Kondaiah)

Radioactive Decay Schemes of Astrophysical Importance: The large relative abundance of stable Br^{79} (50.54%) is attributed in stellar nucleosynthesis to a presumed existence of a relatively shory-lived beta decay pathway from Se^{79} to Br^{79}, which so far has not been detected. What is presently known about Se^{79} decay is shown in the diagram. As shown in the diagram, Se^{79} has its first excited state at 96 keV which is metastable with a half-life of 3.9 min. At the temperatures and pressures existing in stars, it is possible for Se^{79} to be thermally excited to its 3.9 min, 96 keV state,



which is presumed to decay by beta branching to Br^{79} ground-state, in competition with the isomeric gamma transition back to the Se^{79} ground-state, which is long-lived.

The questions of interest here are (1) what amount of beta branching in the decay of 3.9 min Se^{79m} is required to account for the observed abundance of Br^{79} on the basis of present theories of nucleosynthesis, and (2) to what extent, if any, does beta branching occur in 3.9 min Se^{79m} decay?

It is likely that such beta decay in Se^{79m} occurs to the ground-state of Br^{79}, because (a) the beta transition is allowed (1/2- to 3/2-) and has available energy $Q_{\beta^-} = 256 \pm 5$ keV, and (b) the 3.9 min half-life for Se^{79m} appears to be an order of magnitude too short for a 96 keV E3 isomeric transition, compared to the very similar 57 min 103 keV E3 isomeric transition in Se^{81m} decay, suggesting that another major mode of decay, such as β^-, is

present in Se^{79m}.

Work is in progress to detect this beta group from 3.9 min Se^{79m} (prepared by the Se^{78} (n, γ) reaction in the reactor or by the Se^{80} (n, 2n) reaction with 14.4 MeV neutrons), by using a room temperature Si(Li) electron spectrometer. This spectrometer has been calibrated with conversion electrons from Ce^{139}(127 keV), Sn^{113}(364 keV), Cs^{137}(624 keV), and Bi^{207} (482 and 1048 keV). The resolution is about 17 keV FWHM at 364 keV.

A somewhat similar situation occurs in 13 sec Kr^{81m}, for which the existence of a possible EC branching is in question, the ground-state Kr^{81g} having a very long half-life (2.1×10^5 years). This EC branching can be established experimentally by detecting 13 sec Br K_α and K_β x-rays (11.9 and 13.3 keV, respectively) from Kr^{81m} decay, as distributed from 13 sec Kr K_α and K_β x-rays (12.6 and 14.1 keV, resp.). The energy difference between the Kr and Br K x-rays thus is some 700 to 800 eV, which can easily be resolved in our Ge(Li) x-ray photon spectrometer, which gives 437 eV FWHM at the 14.4 keV Co^{57} calibration line. The 13 sec Kr^{81m} can be produced by irradiation of Kr-clathrate either with 14.4 MeV neutrons, Kr^{82}(n, 2n)Kr^{81m}, or with thermal neutrons, Kr^{80}(n, γ)Kr^{81m}, as reported above.

(E. Kondaiah and P. Venugopala Rao)

The decay schemes of $Ag^{106m,g}$ and Rh^{106g} were studied partly in preparation for measurement of the Ag^{107}(n, 2n) cross section at 14.4 MeV. This work is complete and published in Nuclear Physics.

If any abundance anomaly in the Ag^{107}/Ag^{109} ratio exists in meteorities[3,4], any enrichment in Ag^{107} would be attributed to the decay of

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[3] G. Burbidge, Ann. Revs. Nuclear Sci. 12, 563 (1962).

[4] J. H. Reynolds, Ann. Rev. Nuclear Sci. 17, 262 (1967).

7×10^6 year Pd^{107}, which could be formed by neutron-induced reactions. Such Ag^{107} enrichment, however, could in turn be depleted by the $Ag^{107}(n, \gamma)$ reaction with slow neutrons or by $Ag^{107}(n, 2n)$ reaction with fast neutrons above the threshold of 7.61 MeV (produced, for example, by cosmic ray spallation neutrons). Consequently, the measurement of the (n, γ) and (n, 2n) cross sections for both slow and fast neutrons on both Ag^{107} and Ag^{109} and on Pd isotopes is necessary for a proper discussion of this problem. Such measurements with 14.4 MeV neutrons on Ag and Pd are in progress.

(P. Venugopala Rao and R. W. Fink)

The decay scheme of Ga^{72} was studied at Vanderbilt University in a collaboration, and an abstract of a paper presented at the Am. Phys. Soc. is attached.

(P. Venugopala Rao)

Publications: (Supported in some part through the NASA grant NsG-657 and in major part by the U. S. AEC)

"Measurements by Improved Methods of Activation Cross Sections for 14.4 MeV Neutron Reactions," (Review), R. W. Fink, Proc. Conf. on Small Accelerators, Oak Ridge, Tennessee, April 8, 1968.

"Neutron Cross Sections of Br and Rb at 14.4 MeV," P. Venugopala Rao, R. E. Wood, J. M. Palms, and R. W. Fink, Bull. Am. Phys. Soc. 13 (1968).

"14-MeV Neutron Cross Sections of Kr Isotopes," E. Kondaiah, N. RanaKumar, and R. W. Fink, Bull. Am. Phys. Soc. 13, (1968).

"14-MeV Neutron Cross Sections of Si and Zn Isotopes," N. RanaKumar, E. Kondaiah, and R. W. Fink, Bull. Am. Phys. Soc. 13, (1968).

"Levels in ^{106}Pd from Decay of 8.5 day ^{106m}Ag, 24 min ^{106g}Ag,

and 30 sec ^{106g}Rh," P. Venugopala Rao and R. W. Fink, Nuclear Phys. A103, 385 (1967).

"Gamma Decay of $Se^{73m,g}$ and $Se^{81m,g}$ Isomeric Pairs," P. Venugopala Rao and R. W. Fink, Phys. Rev. 154, 1108 (1967).

"Neutron Reaction Cross Sections of Se and Fe at 14.4 MeV," P. Venugopala Rao and R. W. Fink, Phys, Rev. 154, 1028 (1967).

"Decay of Ga^{72} to levels in Ge^{72}," A. V. Ramayya, A. C. Rester, J. H. Hamilton, and P. Venugopala Rao, Bull. Am. Phys. Soc. 12, No. 4, 510 (1967).

2. Capture Gamma Ray Studies - E. T. Patronis, Jr., N. S. Kendrick

Significant improvements were incorporated in the experimental apparatus during the period of September 15, 1967 to March 14, 1968. A 30 cc lithium drifted germanium detector having excellent energy resolution was obtained in order to precisely determine the energies of transitions found in gamma ray spectra. A PDP-8 computer is presently being installed for on-line operation of the experiment and analysis of the experimental data.

E. LIFE SCIENCES

1. Studies on the Growth Dynamics of Protozoans - H. S. Min

The results of the studies on the growth dynamics of protozoans have been directly applied to the study of carbohydrate transport into the cells of insect trypanosomid, Crithidia rileyi. The entrance of carbohydrates into the cells of Crithidia rileyi has been studied with KCN as an inhibitor, using non-metabolizable carbohydrates: L-sorbose, L-xylose, D-xylose, L-arabinose, and D-ribose. The competition between L-sorbose and D-glucose has also been studied. At 0.5 mM external concentration the final intracellular concentration becomes equal to or exceeds the extracellular concen-

tration, and the carbohydrate transport is dependent upon an active transport mechanism. At 20 mM extracellular concentration the maximum intracellular concentration does not exceed the extracellular concentration, and the carbohydrate transport is a facilitated diffusion. The results of inhibition experiments with KCN show that the range of inhibition varies from 9 percent to 34.5 percent and show their maximum inhibition after 16 minutes of exposure. KCN inhibits the uptake of sorbose more than that of any other sugars. There was no sign of inhibition at 20 mM extracellular concentration. The rate of sorbose transport indicates that the competition between sorbose and glucose is greater at higher external concentrations. The entrance of sorbose is sensitive to the presence of glucose and is dependent upon the concentration of glucose present. The results of the studies on the effect of the presence of glucose on the entrance of sorbose show that there is competition between monosaccharides presented simultaneously to the cells and the transport mechanism shows greater affinity for glucose than for sorbose.

These data are interpreted as indicating two mechanisms for carbohydrate entrance: (a) an active transport mechanism, active at low external concentration and dependent upon a supply of metabolic energy; (b) facilitated diffusion, of importance only at high external concentrations.

Publications: Min, H. S. and Y. J. Chung, (1968) Effects of Inhibotor and Competitors on Transport of Carbohydrate in Crithidia rileyi. Submitted to Journal of Cellular Physiology.

III. CONCLUSIONS

The NASA Multidisciplinary Grant NsG-657 continues to stimulate research on the campus and its effectiveness is clearly demonstrated by the number of publications (11), acceptances (5), submissions (2) and presenta-

tions (3) during the six month period, September 15, 1967 to March 14, 1968.

Through the grant graduate students are engaged in quality research activities and, on the average, approximately 35 graduate students receive their financial support from grant funds.

NATIONAL AERONAUTICS AND SPACE ADMINSTRATION

MULTIDISCIPLINARY RESEARCH GRANT

NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

SEMIANNUAL REPORT

September 15, 1968 to March 14, 1969

Report Prepared by

A. L. Ducoffe, Chairman

Georgia Tech Space Sciences Technology Board

May 1, 1969

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

Office of
The Vice President for
Academic Affairs

May 1, 1969

Dr. Francis B. Smith
Assistant Administrator for
University Affairs
National Aeronautics and Space
Administration
Washington, D. C. 20546

SUBJECT: Semiannual Report
September 15, 1968 to March 14, 1969
Multidisciplinary Research Grant NGL 11-002-018

Dear Dr. Smith:

The Georgia Institute of Technology Space Sciences and Technology Board is pleased to submit herewith thirty (30) copies of a semiannual report for Multidisciplinary Research Grant NGL 11-002-018.

We shall be pleased to provide any additional information that you find necessary.

Sincerely yours,

W. L. Bloom
Acting Vice President for
Academic Affairs

WLB/rs

Enclosures

cc: Dr. V. Crawford, Acting President
Mr. H. L. Baker
Members of the Space Sciences and Technology Board

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SEMIANNUAL REPORT

September 15, 1968 to March 14, 1969

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

I. SUMMARY

The National Aeronautics and Space Administration granted the Georgia Institute of Technology $600,000 on June 15, 1964, $300,000 on June 15, 1965, $300,000 on March 15, 1966, $300,000 on March 15, 1967, and $100,000 on March 15, 1968 for the support over six years and nine months of basic scientific research entitled "Multidisciplinary Research in the Space Sciences and Technology."

The grant funds have been used for the first five periods to support an expansion of multidisciplinary research programs in materials and materials processing, transport phenomena, energy conversion, systems, and nuclear processes.

The grant has been administered by the Space Sciences and Technology Board established at the Georgia Institute of Technology. The Chairman of the Board is Dr. A. L. Ducoffe, Director of the School of Aerospace Engineering. The other Board members are H. F. Bauer, Engineering Mechanics; C. H. Braden, Physics; W. O. Carlson, Associate Dean of Engineering; J. W. Hooper, Electrical Engineering; R. H. Kasriel, Mathematics; P. Kelly, Social Sciences; H. A. McGee, Jr., Chemical Engineering; and W. M. Spicer, Director, School of Chemistry.

The fifth grant period runs from March 15, 1968 through March 14, 1969. The present document reports the research results obtained during

the second six months of this period.

An indication of the research activity stimulated by the grant during this reporting period is the publication in recognized journals of 10 papers, the acceptance of 3 others, and the submission of one additional. Twelve papers have been read at scientific meetings. During the present grant period 2 Undergraduate students, 7 Masters students, 19 Ph.D. students and 3 Post Doctorals participated in the research effort.

II. RESEARCH RESULTS

1. High Energy Chemistry

A. Complex Metal Hydrides. High Isp Fuel Components — E. C. Ashby and T. F. Moran

A program designed to illucidate the composition of complex metal hydrides in solution was undertaken beginning in October 1968. The program is concerned with the effect of basic solvents on the composition of complex metal hydrides in solution. The hydrides to be studied are divided into two classes: aluminohydrides and borohydrides. The aluminohydrides to be studied are $LiAlH_4$, $NaAlH_4$, tri-n-octylpropylammonium aluminohydride, $ClMgAlH_4$, and $Mg(AlH_4)_2$. The borohydrides to be studied are $LiBH_4$, $NaBH_4$ and $Mg(BH_4)_2$. The basic solvents to be investigated are diethyl ether, tetrahydrofuran, trimethylamine, triethylamine, tetramethylethylenediamine and triethylenediamine.

Complexes of $LiAlH_4$ with triethylenediamine (TEDA) and trimethylamine of the general formula $LiAlH_4 \cdot$amine have been prepared in ether solvents and characterized by analysis, x-ray powder patterns, and

infrared spectra.

Coordination of the amine has been determined to be occurring on the lithium, for $[(C_8H_{17})_3C_3H_7N]\ AlH_4$ does not form a complex with trimethylamine in toluene. This is consistent with infrared evidence.

Contrary to the observations of Peters, the interation of $LiAlH_4$ and trimethylamine has been shown to give in 100 % yield, bis(trimethylamine)alane and $LiAlH_6$ according to:

$$3LiAlH_4 + 4\ NMe_3 \xrightarrow[1\ month]{Et_2O} Li_3AlH_6 + (NMe_3)_2\ AlH_3.$$

This reaction also occurs to some extent in the absence of solvent.

The TEDA complex seems to be stable in ether, presumably due to its great insolubility. In THF, the reaction of LiH and AlH_3TEDA was found to give $LiAlH_4$ and free amine. No interaction of $LiAlH_4$ and trimethylamine was found in THF.

When THF solutions of TEDA and $ClMgAlH_4 \cdot 4THF$ are mixed, the insoluble AlH_3TEDA is formed and the proposed intermediate, ClMgH, disproportionates to $MgCl_2$ and MgH_2. A tensiometric titration of $ClMgAlH_4 \cdot 2THF$ in toluene indicates the formation of a complex containing two moles of the amine. While only a trace of the bis(amine)alane is formed in this solvent, one can obtain from totally desolvated $ClMgAlH_4$, 55 % yield of the bis(amine)alane by treatment of the hydroaluminate species with excess amine at C° for 6 hours in the absence of solvent.

The titration curve for the trimethylamine-$Mg(AlH_4)_2$ in THF is complex, indicating the formation of adducts up to 3 amines per

$Mg(AlH_4)_2$. There is a break in the curve at 1:1 amine to $Mg(AlH_4)_2$ ratio and another at 3:1 ratio. 42 % of the Al can be recovered as the amine alane after 10 days of reaction.

The first reported complexes of $NaAlH_4$ have been prepared with TEDA and tetra-N,N',N'',N'''methyl ethylenediamine, $NaAlH_4$·amine. These compounds have not produced amine alanes under the conditions thus far tried.

The complete characterization of the cleavage products of the magnesium aluminum hydride species is in progress as well as an evaluation of the effect of solvent on amine abstraction.

The laboratory work was carried out by Dr. Joseph Dilts from Northwestern University who is spending one year in the Hydride Laboratory as a post doctoral assistant.

One technical paper has recently been prepared for publication and will be submitted to "Inorganic Chemistry Journal" within one month.

B. Gaseous Ion-Molecule Reactions — T. F. Moran

Gaseous interactions of reactive species have been examined in an ion beam apparatus in the energy range from 0.75 to 10eV relative kinetic energy. In this work it is possible to produce mass analyzed reactant ions with a narrow kinetic energy distribution and examine the mass, velocity and angular scattering of the reaction products. The dominant interactions in the energy conversion processes of chemically reactive species are found to be elastic scattering, inelastic energy loss into vibrational and rotational degrees of freedom

and atom transfer reactions. The inelastic events involving a change in rotational quantum number are found to undergo a weak oscillatory behavior as a function of kinetic energy while the multi-quantum jump vibrational processes are linear increasing over the energy range studied.

One predoctoral student has been involved in this work. One paper is in preparation.

2. The Growth of Oxide-Metal Composites — A. T. Chapman

The growth of composites containing highly ordered geometries, using unidirectional solidification in eutectic systems, has stimulated much research activity because of the unique and improved behavior of these materials. Most of the systems examined to-date have been metallic; it is the objective of this project to extend the class of materials which can be unidirectionally solidified to oxide-metal (cermet) systems. Current work has concentrated on the search for oxides which may be melted, using high frequency induction heating.

Most of the refractory oxides whose electrical resistivity can be reduced to acceptable levels for induction heating were pressed into cylindrical pellets 0.75 inch in diameter, preheated in air to approximately 1600°C, and exposed to an r.f. field of 27.3 mHz produced by a 10 kw generator. If a molten zone could be established in the pellet, the zone was moved through the pellet at varying speeds to determine if large crystals could be grown, and to establish the experimental condition needed to keep the interior of the pellets molten.

Many nonmetallic materials were inductively melted using the 27.3 mHz unit. Four of the oxides, zirconium dioxide (ZrO_2) stabilized with 5-8 per cent CaO, titanium dioxide (TiO_2), cerium dioxide (CeO_2),

and chromium sesquioxide (Cr_2O_3) will be discussed in some detail.

The stabilized ZrO_2 formed transparent greenish-colored crystals with an oxygen-to-zirconium ratio of 2.00. The material solidified in the cubic system, with a lattice parameter of 5.128 angstroms. Microscopic examination revealed no evidence of a second phase.

The TiO_2 formed small blue-black crystals with an oxygen-to-titanium ratio of 1.99. During the fusion process it underwent a polymorphic transformation from anatase to rutile, with a corresponding increase in theoretical density. The rutile structure is apparently the more stable at room temperature, and no evidence of anatase could be found in the melted material. When the material was heated in air for several hours at 800 - 1000°C, it oxidized to form the yellowish-brown transparent crystals typical of the mineral rutile. A microscopic examination of the crystals prior to the heat treatment revealed the presence of a second, apparently reduced phase. In some areas of the crystals this phase formed continuous parallel rods or fibers, as shown in Figure 1. This is the microstructure that is desired after solidification of oxide-metal systems. The second phase was not evident in the reoxidized specimens.

Cerium dioxide also looks promising as a matrix material. There is practically no change in the crystal structure during melting in air, and the oxygen-to-cerium ratio, though reduced to 1.98, can be restored to 2.00 by heating in air. The crystal size is extremely small, but may be improved considerably by a more controlled cooling process.

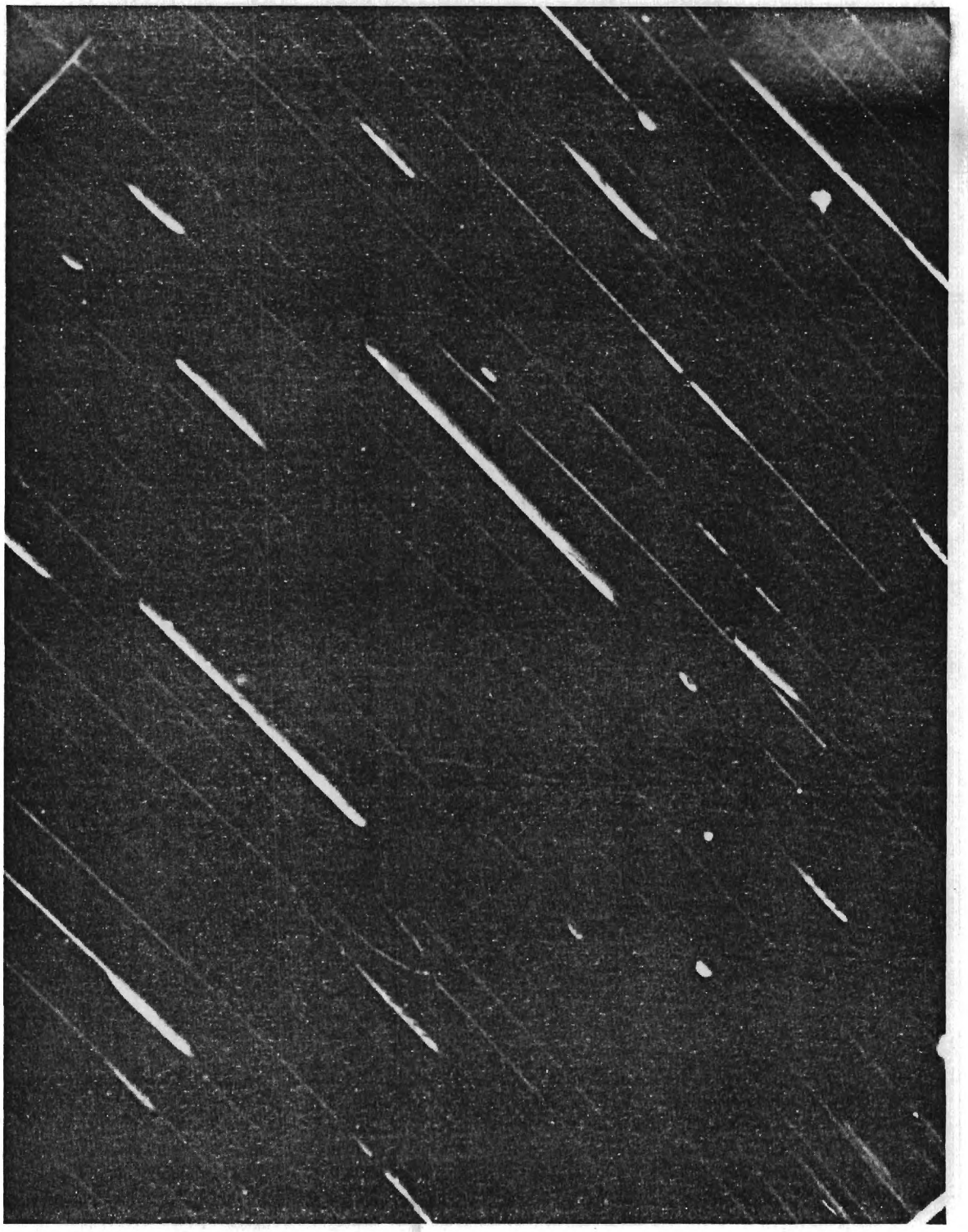

Figure 1. Dark Field View of Induction Melted TiO_2. The bright lines are intersections of the second phase fibers with the surface, the remaining lines are fibers located below the surface (400X).

The chromium oxide experiments, on the other hand, were rather discouraging. It is very difficult to maintain a molten zone in this material, and the resultant crystals are very small. Microscopic examination revealed the presence of metal in the fused material, and x-ray studies verified this as chromium. Large numbers of vapor-grown crystals were evident on the surface of the fused chromium oxide, and the possibility of growing chromium oxide crystals using vapor transport warrants further investigation.

In addition to the induction melting experiments described above, some study of techniques suitable for the analysis of the oxide-metal composites has been undertaken. Figure 2 is a scanning electron micrograph of a UO_2-W cermet grown by the induction melting technique. The sample was grown at the Oak Ridge National Laboratory and the micrograph taken at Georgia Tech. The UO_2 was selectively etched to expose the W fibers and indicates information pertaining to growth conditions can be readily analyzed using the scanning electron microscope.

The scanning microscope studies of the UO_2-W composite will be used during the presentation of a paper entitled, "UO_2-W Cermets Produced by Unidirectional Solidification." This paper will be presented at the Annual Meeting of the American Ceramic Society, Washington, D. C., May 7, 1969.

Two M. S. students, David N. Hill and Christopher Yao, are working on this project. Mr. Hill is currently completing his thesis entitled, "Radio-Frequency Zone Melting of Refractory Oxides."

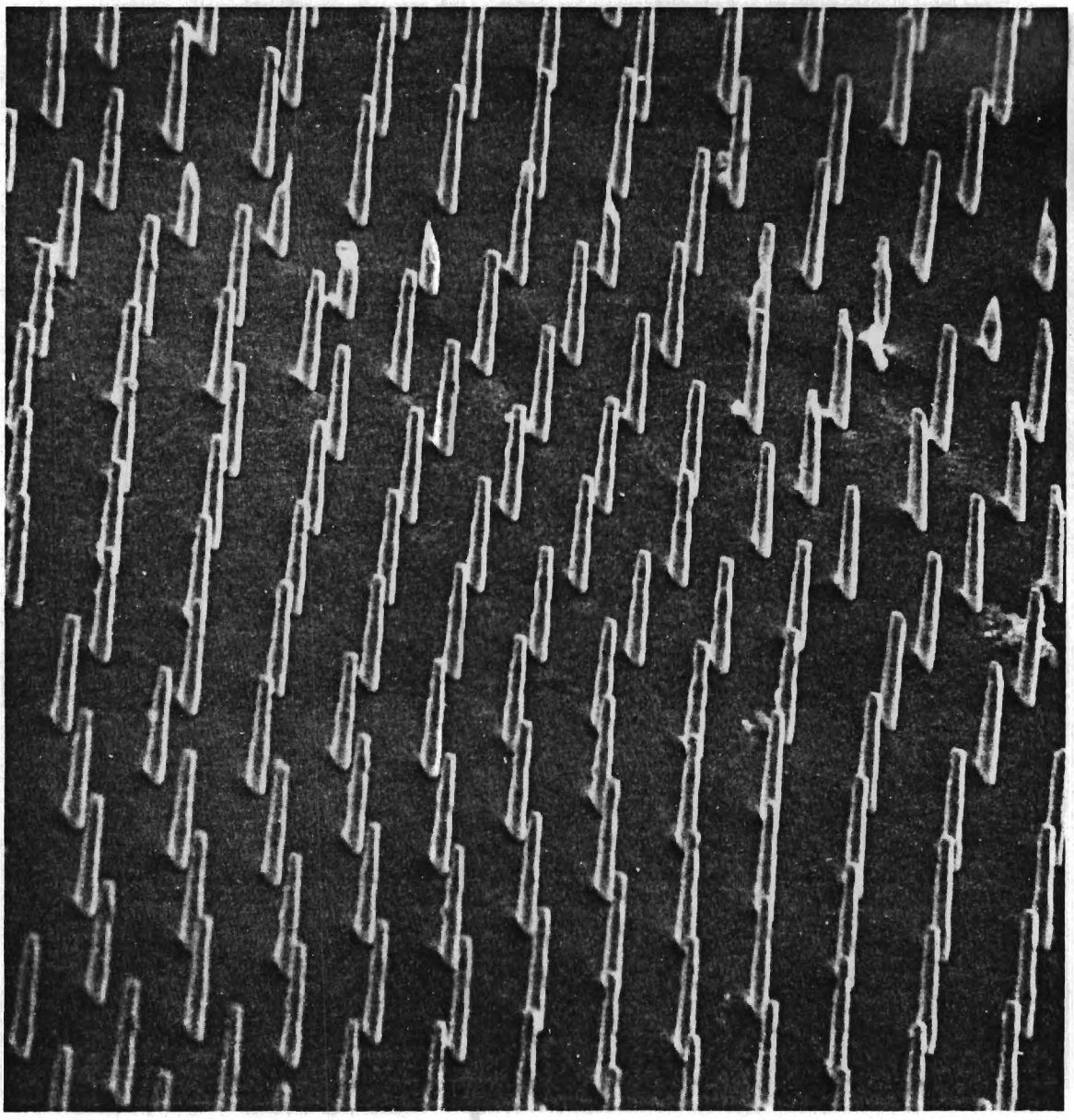

Figure 2. Scanning Electron Micrograph of UO_2-W Cermet showing ordered W fibers protruding from UO_2 matrix. (2000X)

3. Nuclear Astrophysics — R. W. Fink

A. Fast Neutron Reaction Cross Sections of Astrophysical Interest

In stellar interiors, the neutron flux produced through (α,n) reactions or through such reactions as $C^{12}(C^{12},n)$ and $O^{16}(O^{16},n)$ will become thermalized in the keV energy range and will be available for (n,γ) capture reactions. A review by Burbidge[1] suggests many specific cases where fast neutron reactions (up to 15 MeV) at the surface of stars has significantly altered the elemental abundances of the stars.

Neutron activation cross sections for several elements have been measured at thermal (0.0253 eV), 21 keV, and 14.4 MeV energies. A brief summary of the results obtained so far and of work in progress is given below.

Thermal Neutron Cross Sections of Xe, Kr, and Ar Isotopes: By using quinol-clathrate powders of Kr, Xe, and Ar as targets, many (n,γ) cross sections have been determined for the first time with thermal neutrons, and the values of previously measured cross sections have been considerably improved in accuracy. In addition, isomeric cross section ratios have been determined in many cases, from which in the case of Xe the spin cut-off parameters have been calculated. The results for Kr and Xe are published in Nuclear Phys. A120, 329 (1968) and for Ar are accepted and in press for publication in Nuclear Physics.

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[1] G. R. Burbidge, Ann. Revs. Nuclear Sci. 12, 507 (1962).

Neutron Activation Cross Sections of Kr and Xe Isotopes at 21 keV: Some (n,γ) cross sections of Kr and Xe isotopes for 21 keV neutrons--the energy region of interest for nucleosynthesis in stellar interiors--were investigated by using the Oak Ridge National Laboratory 3 MeV Van de Graaff accelerator with $Li^7(p,n)$ neutrons, in collaboration with Drs. J. H. Gibbons and R. L. Macklin. Since the neutron output of 30 keV neutrons is only about 10^6 n/sec, and since the cross sections are expected to be in the region of 10 to 100 millibarnes, large rare gas clathrate powdered samples contained in polyethylene cones (containing PbI_2 neutron monitor) were irradiated and counted with our 10 cm^3 Ge(Li) detector. However, as the quinol clathrate compounds and the polyethylene cones contain carbon and hydrogen, the thermalization of keV neutrons in these samples is serious. The average energy of the initial 30 keV neutrons is reduced to about 21 keV, and there is considerable thermalization of 0.025 eV. A Monte Carlo computer calculation was performed to determine the neutron spectrum inside the samples. This calculation showed that it is not possible to get a good value for the keV cross sections in these measurements. We therefore propose the use of liquified rare gases as samples for measurements in the keV neutron region. At present, there are no further plans for carrying out such measurements, owing to lack of funds for conducting extensive measurements at Oak Ridge.

Neutron Cross Sections at 14.4 MeV for Xe, Kr, and Ar Quinol-clathrates: The (n, 2n), (n,p), and (n,α) reaction cross sections of Xe, Kr, and Ar isotopes have been measured at 14.4 ± 0.3 MeV using mixed quinol-clathrate powders and Ge(Li) gamma spectrometry. The

results for Xe and Kr have been published in Nuclear Phys. A120, 337, (1968). The result for Ar has been accepted and is in press for publication in Nuclear Physics.

Neutron Cross Sections at 14.4 MeV for Si and Zn Isotopes: These cross sections are of value for the 14 MeV neutron activation analysis of lunar surface, by using small sealed portable 14 MeV neutron generators on lunar probes (e.g., Surveyor). We have measured the $Si^{28}(n,p)Al^{28}$(2.3 min) cross section with an accuracy sufficient to be used as a standard cross section. This reaction has special interest as a monitor for other short-lived products. The results for Si and Zn isotopes have been published in Nuclear Phys. A122, 679 (1968).

(n,2n) Cross Sections at 14.4 MeV in the Region of Z = 40 - 60: Gardner[2] and Pearlstein[3] have made extensive calculations to predict (n,2n) cross sections at 14 - 15 MeV semi-empirically. Their predictions differ from one another very much for the light isotopes of the elements, particularly in the region of Z = 40 - 60. There are few previous experimental measurements of these cross sections because of the generally low abundances of the light isotopes of each element; the few existing values differ very much, so that no conclusions can be drawn from them. Therefore, measurements are now in progress to measure accurately all of the (n,2n) cross sections at 14.4 ± 0.3 MeV for elements between Z = 40 and 60, by using the mixed

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[2] D. G. Gardner, U. S. Atomic Energy Commission Report, UCRL-14575 (1966) (Unpublished).

[3] S. Pearlstein, Nuclear Data A3, 327 (1967).

powder--Ge(Li) method. From the experimental precision values a better normalizing procedure in the semi-empirical predictions[2,3] will be attempted, in order to get better estimates of the cross sections which cannot be measured by gamma detection. Some of the results so far obtained will be reported at the American Physical Society meeting April, 1969, in Washington, D. C.

Cross Sections for 14.4 ± 0.3 MeV Neutrons of Br, Rb, and Sr Isotopes: The following cross sections have been determined, and those for certain of the Rb isotopes will be reconfirmed before publication. A manuscript for publication of these results is in preparation.

Reaction	Half-life	Measured Gamma (keV)	f_d (γ/dis)	Cross Section (millibarns)
$Br^{79}(n,2n)Br^{78}$	6.5 m	614	0.13	741 ± 74
$Br^{79}(n,\alpha)As^{76}$	26.4 h	559	0.39	20 ± 2
$Br^{81}(n,2n)Br^{80m}$	4.52 h	618[a]	0.066	737 ± 74
$Br^{81}(n,2n)Br^{80g}$	17.7 m	618	0.066	391 ± 39
$Br^{81}(n,\alpha)As^{78}$	90 m	614[b]	0.42	19 ± 2
$Br^{81}(n,p)Se^{81m}$	18.6 m	103	0.08	19 ± 2
$Rb^{85}(n,2n)Rb^{84m}$	20 m	250, 464	0.60, 0.35	478 ± 48
$Rb^{85}(n,2n)Rb^{84g}$	33 d	880	0.74	414 ± 41
$Rb^{85}(n,p)Kr^{85m}$	4.4 h	150	0.78	4.1 ± 0.4
$Rb^{85}(n,\alpha)Br^{82}$	35.34 h	553, 777	0.73, 0.83	4.9 ± 0.5
$Rb^{87}(n,2n)Rb^{86}$	18.7 d	1078	0.09	973 ± 97
$Rb^{87}(n,p)Kr^{87}$	76 m	405	0.81	4.9 ± 0.5
$Rb^{87}(n,\alpha)Br^{84g}$	31.7 m	880	0.42	1.8 ± 0.2
$Sr^{84}(n,2n)Sr^{83}$	32.4 h	380	0.35	357 ± 36
$Sr^{86}(n,2n)Sr^{85m}$	70 m	231	0.83	247 ± 25
$Sr^{87}(n,n')$ + $Sr^{88}(n,2n)$ } Sr^{87m}	2.83 h	388	0.78	232 ± 23
$Sr^{88}(n,p)Rb^{88}$	17.8 m	898	0.15	13 ± 1.5
$Sr^{88}(n,\alpha)Kr^{85m}$	4.4 h	150	0.78	13 ± 1.8

a from Br^{80g}

b the decay scheme was investigated; abstract attached

B. Radioactive Decay Scheme Studies

Beta Decay Branching in Se^{79m} Decay: The astrophysical significance of this problem was discussed in detail in the previous report. The experimental result is given here. A room temperature silicon electron detector (resolution 17 keV FWHM at 662 keV conversion electrons) was used to study the electron spectrum from 3.9 min Se^{79m}, which was produced by thermal (n,γ) reaction of 90% enriched Se^{78}. A search was made for possible (1/2- → 3/2-) allowed beta-decay branching from Se^{79m}. Only the conversion electrons from the 96 keV E3 isomeric transition were observed. Owing to masking by the continuous beta spectrum of 18 min Se^{81g}, also present, a sensitive lower limit on the beta branching from Se^{79m} could not be set. However, such a beta branch must be lower than about 0.01 β^-/dis in Se^{79m} decay.

K-shell Conversion Coefficient in the 40.58 keV Transitions in Mo^{99} Decay: This problem is completed and the results are in press for publication in Nuclear Physics.

Personnel:

Prof. R. W. Fink, Principal Investigator.

Dr. N. RanaKumar, Postdoctoral Research Associate, under NASA grant support from December 1, 1968 to June 30, 1969. Will terminate June 30, 1969 unless additional funds are made available.

Prof. E. Kondaiah, NSF Senior Foreign Scientist and Visiting Professor, 1967/68. Terminated September 15, 1968.

Dr. P. Venugopala Rao, supported summer, 1968, from this NASA grant. Presently Assistant Professor of Physics, Emory University,

Atlanta, Georgia from where Dr. Rao continues his research collaboration with this project.

Mr. W. Lu, supported by a fellowship from Republic of China, Taiwan, but works toward Ph.D. on this project (cross section Z = 40 - 60).

Papers Presented at Meetings:

R. W. Fink:

Invited paper: "Measurements by Improved Methods of Activation Cross Sections for 14.4 MeV Neutron Reactions."

Proceedings Conf. on Research & Educational Uses of Small Accelerators, Oak Ridge, Tennessee, April 8, 1968, U.S. AEC Publication CONF-680411 October, 1968.

American Physical Society, Miami Beach, Florida, November, 1968, "Thermal Neutron Activation Cross Sections for Xe Isotopes," R. W. Fink, E. Kondaiah, and N. RanaKumar, Bull. Am. Phys. Soc. 13, 1422 (1968).

N. RanaKumar:

American Phys. Soc., Washington, D. C., April, 1969 (to be presented), "Neutron Activation Cross Section for (n,2n) Reactions at 14.4 MeV for Elements with Z = 40 - 60," N. RanaKumar, W. Lu, and R. W. Fink, Bull. Am. Phys. Soc. 14, in press (1969).

American Phys. Soc., Washington, D. C., April, 1968, "Neutron Activation Cross Sections at 14.4 MeV for Kr and Xe Isotopes," E. Kondaiah, N. RanaKumar, and R. W. Fink, Bull. Am. Phys. Soc. 13,

602 (1968).

Am. Phys. Soc., Miami Beach, Florida, November, 1968, "Neutron Activation Cross Sections at 14.4 MeV for Xe Isotopes," N. RanaKumar, E. Kondaiah, and R. W. Fink, Bull. Am. Phys. Soc. 13, 1422 (1968).

Am. Phys. Soc., Washington, D. C., April, 1968, "Neutron Activation Cross Sections at 14.4 MeV for Si and Zn Isotopes," N. RanaKumar, E. Kondaiah, and R. W. Fink, Bull. Am. Phys. Soc. 13, 602 (1968).

P. Venugopala Rao:

Am. Phys. Soc., Washington, D. C., April, 1968, "Neutron Cross Sections for Br and Rb at 14.4 MeV," P. V. Rao, R. E. Wood, J. M. Palms, and R. W. Fink, Bull. Am. Phys. Soc. 13, 602 (1968).

Am. Phys. Soc., Miami Beach, Florida, November, 1968, "Levels in Se^{78} Populated by the 90 min Decay of As^{78}, "P. V. Rao, Bull. Am. Phys. Soc. 13, 1450 (1968).

Publications:

"Thermal and 14.4 MeV Neutron Activation Cross Sections of Argon," N. Ranakumar, E. Karttunen, and R. W. Fink, Nuclear Phys. (in press, 1969).

"K-shell Conversion Coefficient of the 40.58 keV Transition in Mo^{99} Decay," N. RanaKumar, R. W. Fink, and P. V. Rao, Nuclear Phys. (in press, 1969).

"Thermal Neutron Activation Cross Sections for Kr and Xe Isotopes," E. Kondaiah, N. RanaKumar, and R. W. Fink, Nuclear Phys. A120, 329 (1968).

"Neutron Activation Cross Sections for Kr and Xe Isotopes at 14.4 MeV," E. Kondaiah, N. RanaKumar, and R. W. Fink, Nuclear Phys. A120, 337 (1968).

"Neutron Activation Cross Sections at 14.4 MeV for Si and Zn Isotopes," N. RanaKumar, E. Kondaiah, and R. W. Fink, Nuclear Phys. A122, 679 (1968).

"Measurements by Improved Methods of Activation Cross Sections for 14.4 MeV Neutron Reactions," R. W. Fink, Proc. Conf. on Res. and Educational Uses of Small Accelerators (Oak Ridge Assoc. Univ., 1968); p. 30ff.

"Levels in Se^{78} from Decay of As^{78} and Br^{78}," P. V. Rao, Bull. Am. Phys. Soc. 13, 1450 (1968).

"Neutron Cross Sections for Br and Rb Isotopes at 14.4 MeV," P. V. Rao, R. E. Wood, J. M. Palms, and R. W. Fink, Bull. Am. Phys. Soc. 13, 602 (1968) and to be published.

4. Study of Plasma Flow Around an Ionospheric Vehicle — A. B. Huang

Objectives of the Research: It is intended to provide the basic theoretical study for solutions of the nonlinear plasma-ionospheric vehicle interaction problem. The results are essential in the prediction of satellite decay times (the determination of particle drag on vehicle), the use of measured rate of decay to gain information about the properties

of the upper atmosphere, vehicle tracking, and radar detection, etc.

Brief Description: The problem was formulated from the molecular approach of kinetic theory using the nonlinear Boltzmann equation and the Poisson equation as the fundamental governing relations and using the discrete ordinate method as a tool. This formulation was first applied to the neutral particle case in order to gain some confidence. The results were excellent in accordance with the existing experimental data. The formulation is being applied to the plasma case. Some good results have been obtained.

Names of Graduate Students Involved:

Victor Y. C. Young (Ph.D. Program)

C. S. Lu (Ph.D. Program)

Publications: "Nonlinear Rarefied Couette Flow with Heat Transfer," by A. B. Huang and D. L. Hartley, Phys. of Fluids 11, 1321-1326 (1968).

"Nonlinear Rarefied Rayleigh's Problem," by A. B. Huang and D. L. Hartley, AIAA Journal 6, 2023-2025 (1968).

"Kinetic Theory of the Sharp Leading Edge Problem in Supersonic Flow," by A. B. Huang and D. L. Hartley, Phys. of Fluids, 12, 96-108 (1969).

Presentation of Papers: "Kinetic Theory of the Sharp Leading Edge Problem II. Hypersonic Flow," presented at the 19th International Astronautical Congress, New York, Oct. 13-19 (1968).

"Kinetic Theory of the Rarefied Supersonic Flow Over a Finite Plate," presented at the 6th International Symposium on Rarefied Gas Dynamics, MIT, Boston, July 22-26 (1968).

5. Construction and Characterization of Solutions of Optimal Control Problems of Distributive Systems — A. L. Mullikin

The objective of the research was two-fold:

(1) Given the state equation

$$\dot{x}(t) = f(x(t), u(t), t)$$

where f is nonlinear but certain weak convexity conditions are satisfied, provide a characterization of optimal control (i.e., necessary and sufficient conditions for u^* to be an optimal control) under either the requirement of minimum effort or of a final-value constraint. The authors took minimum effort to mean that the expression

$$\int_0^T [\, \langle Qu, u \rangle + \langle Kx, x \rangle \,] \, dt$$

is to be minimized with respect to u, where Q and K are positive bounded linear operators; and final-value constraint to mean that

$$|| \, x_0 - x(t) \, ||$$

is to be minimized with respect to u where x_0 is a fixed element in the state space and T is the final time.

(2) Extend gradient minimization methods in function spaces, particularly the method of steepest descent and the conjugate gradient method to numerical computations of such optimal control

problems for linear and certain nonlinear controls.

Work on this project was performed primarily during the summer of 1968. Most of this time was devoted to review of literature to the end that available techniques could be applied to the problem. Some minor results were obtained, but these have not been submitted for publication.

6. Vibration and Stability of Distensible Fluid Lines Carrying a Pulsating Incompressible Liquid — J. Siekmann

Objectives of the Research: Utilization of Fluid Transmission Lines in automatic control, liquid-propellant rocket and other systems requires knowledge of their dynamic response. In this study the symmetric and asymmetric modes of propagation for a viscous liquid in a cylindrical elastic conduit will be investigated.

Description of the Work Performed: In order to overcome some of the mathematical difficulties of the Navier-Stokes equations, a classical similarity solution to the equations of motion is sought. The idea behind this approach is to find a suitable transformation so that the set of partial differential equations may be reduced to a set of ordinary differential equations that are functions of a single independent variable. It is hoped that this set of equations can then be integrated, either analytically or numerically, to yield the solution of the problem.

Results: Based on the works of Gol'dshtik, Kidd and Farris, Schwiderski and Lugt, the complete Navier-Stokes equations in a cylindrical coordinate system are reduced to a set of nonlinear ordinary differential equations by appropriate similarity transformations. Methods of

solutions are under investigation. Difficulties in the treatment of the boundary conditions, arising from the elastic-flexible conduit, are studied.

Graduate Students Supported by this Project:

Mr. Shih-Chih Chang, Ph.D. student.

Publications: "On the Damping of a Sloshing Liquid by Movable Devices," by J. Siekmann and Shih-Chih Chang, submitted to Acta Mechanica for consideration for publication. Although the content of this paper is not directly related to the topic of the above research project, this study nevertheless yields some valuable information about the damping effectiveness of membranes and plates immersed in liquid.

7. Atomic and Magnetic Ordering in Transition Metal Alloys — S. Spooner

Objectives: This multidisciplinary program has as its objective to understand the relationship between ordering phenomena and the physical properties of technically significant magnetic alloy systems. By coordinating solid state physics and metallurgical studies of selected alloys, a fundamental understanding motivated by practical objectives is sought. The work is centered on experimental studies using Mössbauer spectroscopy and neutron diffraction while theoretical studies of the statistical mechanics of ordering is carried on in parallel. The particular alloy system of iron-cobalt has been selected for its intrinsic scientific as well as practical interest. A subsidiary study of the ordering effect on mechanical working of nickel-maganese alloys has also been supported in part.

Description of Work: The Mössbauer spectroscopy work has proceeded rather well with the use of quenched alloy powders. Using a special quenching technique it has been possible to characterize changes in the spectra as a function of temperature of the sample prior to quenching. Significant changes in the behavior of the hyperfine field have been seen near 550°C and 720°C where other investigators have observed anomalies. The intention is to continue these studies with an exploration of composition dependence of these effects in the hope of correlating new observations with some of the less definitive work of other research investigators (especially specific heat measurements).

Neutron diffraction work has been useful in characterizing the state of order as a function of heat treatment and mechanical working, but because of the limited effectiveness of the powder diffraction techniques in obtaining the magnetic structure, modifications of the equipment to include polarized neutron beam techniques have been started. In addition, planning for a high temperature diffraction furnace is nearly complete. With these changes, the important relationship between atomic arrangements and magnetic structure can be assessed more quantitatively and the temperature characteristics (including kinetic factors) of the atomic ordering reaction of approximately 720°C can be measured for comparison with statistical mechanical theories of ordering processes.

Results: Mössbauer spectra have been obtained from powdered samples of a FeCo alloy after various heat treatments and mechanical deformation. Neutron diffraction patterns were used to indicate the degree of order in a well ordered sample and a completely disordered sample. These samples were then used as reference points in a series of

Mössbauer measurements in which the disordered sample was subsequently annealed and quenched from temperatures between 500°C and 850°C. In particular, the spectral splitting and line-widths measured at room temperature were determined as a function of temperature. The splitting of the outer peaks increased from 10.8 mm/sec to 11.4 mm/sec on going from the lowest to highest quench temperature, representing atomic order and disorder respectively. These values are in the range of values measured by other workers but are reversed with respect to the degree of order. A plot of the hyperfine splitting versus quench temperature reveals a change in slope at 730 ± 5°C corresponding to the atomic order transition. A second change in slope was found at 550°C corresponding to an anomalous phase transition which remains unexplained at present.

The changes in hyperfine field are presently being interpreted on the basis of a model in which order-dependent and order-independent terms add to the hyperfine field present at the iron nucleus. The effect of order is assumed to reside in the changing of first neighbor atom occupations; the ordered configuration calls for eight cobalt atom neighbors while the disordered configuration calls for only four. The order-independent term is considered to be some form of background effect associated with the conduction electrons and is assumed to be composition dependent. As yet it is not clear how these observations are related to the changes in magnetic moment recently measured at Argonne National Laboratory. The 3 per cent decrease in hyperfine field upon ordering will have to be found consistent with a corresponding 3 per cent increase in the iron local moment in this equiatomic alloy.

Neutron diffraction studies of the effect of ordering and

mechanical working upon each other is being studied in the nickel-manganese as well as in the iron-cobalt system. It is anticipated that in this FCC alloy system that a significant change in stacking fault energy should occur with ordering. This, in turn, can be expected to modify the nature of the deformation texture which results from rolling of partially ordered alloys. In addition, the result of deformation is known to destroy the ferro-magnetic properties of this system by virtue of the induced changes in the near-neighbor atomic configurations.

The mechanical properties of the iron-cobalt system are quite different. It is known that the mode of deformation changes with a rather small decrease in order. Our findings show that the deformation encountered in grinding powders is adequate to induce total disorder of atomic arrangements in a highly ordered specimen. Since the alloy is normally brittle under standard deformation processing (thus having little plastic ductility) it is surprising that so extensive a disordering is possible in this mode of deformation. It appears that the relationship between plastic deformation and state of atomic order are quite different between the two systems since a 38 per cent reduction in rolling of the nickel-manganese alloy shows only gradual reduction of atomic order. A possible explanation may be found in the consideration of detailed deformation processes in which initial deformations are adequate to induce disordering which in turn leads to increased ductility and thus a complete destruction of the ordered configurations.

Conclusions: The hyperfine field measured at the iron nucleus with Mössbauer spectroscopy has been found to decrease upon ordering. Furthermore, these changes have been used to delineate two-phase trans-

formations in the equiatomic alloy at 550°C and 730°C.

Neutron diffraction has been used to assess the degree of long-range order in an equiatomic iron-cobalt alloy (BCC) and in a Ni_3Mn alloy (FCC). The mechanical working on each alloy induces atomic disorder which slightly decreases the magnetization in the iron-cobalt alloy and is known to totally destroy ferro-magnetism in the nickel manganese alloy.

Graduate Students:

Ben DeMayo	(Ph.D.)
Sam Scales	(Ph.D.)
Joe Saltzberg	(M. S.)
J. W. Lynn	(M. S.)
P. S. Keith	(M. S.)

Publications: B. DeMayo, D. W. Forester, and S. Spooner, "Effect of Atomic Ordering on Hyperfine Field in Fe (50-50) Co." (in preparation).

Presentation of Papers: B. DeMayo, D. W. Forester, and S. Spooner, "A Mössbauer and Neutron Diffraction Study of Atomic Order in Fe (50-50) Co," Bull. Am. Phys. Soc. 13, 1706 (1969).

B. DeMayo, D. W. Forester and S. Spooner, "Mössbauer and Neutron Diffraction Measurements of Atomic Ordering Effects in Fe (50-50) Co," Bull. Am. Phys. Soc. 14, 99 (1969).

8. A New Technique for Detection of Infrared Radiation -

A. L. Stanford

Objectives of the Research: To investigate materials and fabrication techniques for utilizing the pyroelectric effect as a thermal detector.

Description of Work Performed: During the past report period, the discovery of ferroelectricity (and therefore, the concomitant pyroelectricity) in the nucleic acid RNA has turned the attention of the investigators to the possibilities associated with biological materials, natural or synthetic, as detectors of radiation. The pyroelectric nature of RNA has been established, but a suitable crystalline form as a detector has not been found.

Results: The ferroelectric nature (and thus the pyroelectric nature) of sodium ribonucleate has been demonstrated and is being pursued as a detector material.

Conclusions: None as yet.

Publications: A. L. Stanford, Jr. and R. A. Lorey, "Evidence of Ferroelectricity in RNA," Nature 129, No. 5160, 1250-1251 (1968).

Presentation of Papers: Stanford, A. L., Jr., "Ferroelectric Hysteresis in RNA," Invited paper presented to Southeastern Section of American Physical Society at University of Georgia, October 9-11, 1968.

9. The Physical and Functional Aspects of Integrated-Circuit Technology - K. L. Su

Objectives of the Research:

(1) To devise new and better ways of forming integrated-circuit functional modules. To explore the possibility of using these modules in network synthesis.

(2) To characterize material and device properties for active thin film structures. To develop system design concepts for the thin film structures that will extend the capability of micro-miniaturization to higher frequencies.

(3) To investigate semiconductor interface phenomena as they affect device characteristics.

Description of Work Performed: In the circuit phase of the research the following work has been performed:

(1) The realization of the nullor by the integrated-circuit operational amplifiers has been studied in detail. It has been found that the availability of this device, especially in the ungrounded (floating) form will enable one to synthesize many new devices formerly only realizable in approximate forms with transistors.

(2) The realization of the ideal transformer with integrated-circuit operational amplifiers has been attempted. One scheme is to connect a current-controlled current source in the series-parallel manner with a voltage-controlled voltage source. This scheme will allow only one form of excitation of each side of the transformer. The other scheme is to connect the two controlled sources in parallel through a nullor. The nullor will allow the two controlled sources to function

independently without interfering with each other.

(3) The concept of the universal-impedance converter has been developed. A universal-impedance converter is a two-port device whose current and voltage ratios can have any polarities and signs. The realization of this converter can be achieved by extending the schemes in (2) above such that the ratios are not restricted to those realizing an ideal transformer.

(4) Possible synthesis techniques using the positive impedance converter (PIC) as the active element has been investigated. Some sensitivity study has been conducted.

The work performed in the materials and device area may be divided into six parts. These parts are:

(1) Fabrication of thin germanium films using rf-bias sputtering techniques--Several evaporations were made of germanium over an entire substrate earlier in the program during this period. The first two runs were on glass substrates and the third on sapphire. The germanium on the sapphire was completely polycrystalline even through the substrate surface appeared to be single crystalline. The crystalline characterization was determined by using the grazing electron diffraction technique. The film on the sapphire was 2 microns thick as measured by multiple beam interferometry. This film was obtained in about 40 minutes of sputtering on a 250°C substrate. It is anticipated that a slower sputtering rate and a higher substrate temperature will be required for epitaxial formation.

(2) Development of fabrication technique to realize ultra-small gaps--The device fabrication requirements indicate a need for obtaining ultra-small gaps between metallizations. For example, the gap between the anode and cathode in the Schottky barrier diode must be smaller than 1 micron. An invention disclosure has been submitted on a technique to accomplish this. Several trial gaps were made to evaluate the technique. The results indicate that gaps of less than 1 micron are easily fabricated with good accuracy. This process employs the growth of an oxide mask by anodization which separates the anode and cathode metal layers. Subsequent removal of the oxide by selective etching produces the gap. Optical and scanning electron micrographs clearly reveal the resolution of the technique.

(3) Sapphire substrate preparation and evaluation--In order to repeatably grow single-crystal epitaxial layers on a substrate, it is necessary to have a highly polished and single crystal substrate surface which can be evaluated before deposition takes place. The purity of the substrate is important but the surface texture is even more important for epitaxial requirements. A hydrogen firing furnace has been constructed and put into operation for annealing the substrates. The furnace is capable of controlled firings in hydrogen up to 1300°C. X-ray source image distortion (SID) techniques indicate the sapphire to be highly single crystal in nature and oriented with the basal plane parallel to the surface. Low angle reflection diffraction, however, shows the surface to be polycrystalline in nature.

(4) Drift mobility and carrier lifetime--Bulk and thin film measurements.

(5) Resistivity and Hall mobility measurements--Bulk and thin film measurements.

(6) Microwave integrated circuit and materials survey-- A continuing effort.

In the semiconductor interface investigation the following work has been performed:

(1) A study on the characterization of devices and the understanding of the fundamental physics of interfaces has been conducted. Several solid-state devices of the Metal-oxide-semiconductor (MOS) or Metal-insulator-semiconductor (MIS) type have been identified. The effects of fast surface states, mobile impurity ions and traps ionized by radiation on the current-voltage curves have been reviewed.

(2) Experimental study was made of the current-voltage characteristics of a MOS structure and transducer action was observed with the application of pressure, temperature, and light.

(3) A study on methods to determine the surface charges in MOS devices by measurements of current-voltage characteristics was conducted.

(4) A survey on literature pertaining to internal photoemission was made.

Results: In circuits, the following results were obtained -

(1) Several new methods of realizing the ungrounded nullor using integrated-circuit element have been developed. These circuits use both the single-ended and the differential-input single-output operational amplifiers. Experimental results show that these circuits do

perform satisfactorily.

(2) Two ideal transformer circuits have been breadboarded and tested. Results show that these circuits function well up to 500 KHz.

(3) Modification of the ideal-transformer circuits to function as the universal-impedance converter is in progress. Experimental results here are comparable to those of ideal transformer circuits.

(4) A technique for realizing any transfer function that has only simple negative real-axis zeros using only resistances, capacitances, and one PIC has been developed. Specifically, a circuit for realizing a second-order function has been studied in detail. It has been shown that for this circuit the Q sensitivity can be made zero. This result shows the usefulness of the PIC as an active element.

In materials and devices:

(1) Polycrystalline films of germanium have been grown on sapphire.

(2) Ultra-small gap fabrications have been realized.

(3) Preliminary measurements have indicated a need for certain indicated changes in material properties (surface texture) and processing parameters.

In interfaces; a MOS transducer which can be used to measure mechanical pressure or force, temperature, and light in digital form has been constructed and tested. The experimental results of this device have been published.

Conclusions:

(1) Circuits--The integrated-circuit realizations of the nullor, the ideal transformer, the universal-impedance converter, and the positive-impedance converter have been shown to be feasible both theoretically and experimentally. Preliminary results show that the positive-impedance converter is an excellent element for active network synthesis. This conclusion appears to have opened up a new area for further investigation.

(2) Materials and devices--No terminal conclusions can be drawn at this time other than those relating to the gap fabrication scheme. Work will continue on the fabrication of germanium and gallium arsenide films with epitaxial properties for active device fabrication. It is anticipated that the substrate problem will be resolved shortly. A statistically designed experiment of fabrication parameter variation is being planned to optimize the evaluation of parameter dependence and interaction on the epitaxial process. A microwave system design and analysis is planned based on material and device characterizations.

(3) Interface--It became clear that before further device type measurements were made it would be necessary to examine in greater detail the fundamental physics of the interfaces involved. This would involve photoemission measurements in which electrons are excited above the semiconductor-insulator barrier and collected at the metal electrode, and similar measurements where electrons are excited above the metal-insulator barrier and collected at the semiconductor.

Students:

	Department	Level
R. J. Mitchell	Physics	Senior
J. H. Taylor	Physics	Senior
B. A. Bond	E. E.	M.S.
R. S. Gordy	E. E.	M.S.
D. R. Cobb	E. E.	Ph.D.
D. W. Covington	E. E.	Ph.D.
F. L. Grismore, Jr.	E. E.	Ph.D.

Publications: C. K. Kuo, M. E. Sikorski, and E. J. Scheibner, "MOS Transducers with Digital Measurement Capability." IEEE Proc., vol. 56, pp. 1599-1600, September 1968.

10. Collisional De-excitation of Atomic Particles — E. W. Thomas

Objective: The objective of the work is the study of mechanisms whereby light atoms of some keV energy interact with atmospheric gases. In particular, it is intended to study the collisions of excited H and He atoms which result in the stripping of the excited electron. Protons and alpha particles from the sun are responsible for inducing certain types of auroral phenomena. The presence of these fast moving particles may be diagnosed by observing doppler shifted emission which is produced when the projectiles are neutralized through the process of charge transfer into an excited state. It has been suggested that collisional destruction of the excited atom before it emits a photon may seriously affect the

quantitative validity of the diagnosis which is based on such measurements.

The experiments are designed to investigate the process of formation and destruction of excited atoms at projectile energies of 5 to 30 keV. Work will be directed primarily at the metastable states of the neutralized projectiles since this greatly simplifies the problems of detection. Data from this study can be readily extrapolated to higher levels by well established theoretical rules.

The program will determine cross sections for the formation of the metastable state of hydrogen as protons and ground state atoms transverse targets of helium and nitrogen. Measurements will be made as a function of the distance of closest approach between the colliding atoms. Also the experiments will be carried out using metastable beams and monitoring their destruction. The cross section for stripping the excited electron into the continuum will be measured directly.

Description of the Work Performed: It has been reported previously that the program has been much broadened beyond the original concept through an infusion of financial support from Georgia Tech sources. Therefore, the program is more comprehensive than originally envisaged and is also proceeding more slowly. The recent six month period has been devoted to the final assembly of the apparatus and carrying out a rather detailed examination of the operating characteristics of certain component parts of the experimental arrangement.

The experimental research program will require that low energy ion and neutral beams be monitored continuously. Some of these beams will be of very low intensity. Traditional detectors for these purposes have certain disadvantages associated with poor sensitivity and loss of sensi-

tivity on exposure to air. A relatively new device known as a "channeltron" multiplier has found much application in satellite and rocket borne research experiments for detecting ions, electrons, neutral particles, and photons. This device is ideally suited to the present research programs since it is of small size, requires reasonably low operating voltages, and is reputed to be insensitive to exposure to air. Unfortunately, the published information on the device is mainly concerned with its use in qualitative experiments. There was insufficient evidence that the device could be used as an absolute detector at the low projectile energies associated with this proposed research. In view of the potential utility of this type of device to the present program and also to other work sponsored under this NASA grant (Dr. T. F. Moran, Chemistry), it was decided to carry out a fairly thorough test of these devices. This objective has been fully accomplished and is now terminated. Considerable valuable information was obtained on the operation of "channeltrons" for quantitative detection of low intensity fluxes of particles.

The major objective of the program which is to study collisional rearrangement problems is being commenced at the present time. All equipment for the initial stages of the experiment is on hand at the present time.

During the course of the development of the equipment, considerable attention has been paid to the theory of the operation of the experiment. As a result, certain systematic errors have been discovered in published data.

Results: At the present time, no results have been acquired on the primary objectives of the program.

A considerable effort has been applied to the study of channeltron electron multipliers of four different types. This has demonstrated that certain of the channeltron configurations are capable of detecting H^+ at energies as low as 0.5 keV and Ar^+ at energies as low as 2 keV. These results may be readily applied to the prediction of operating characteristics for ions of intermediate mass. Furthermore, there is a very important limitation on the count rate which these devices can handle without error due to the loss of signal. This limit can be as low as 5×10^3 counts per second in one type. Techniques have been developed for ensuring that the detection efficiency over the whole of the active aperture of the device is uniform. These results indicate the usefulness of the device and also show very definitely that certain designs, particularly those sold by Mullard, Inc., have some very severe limitations. These results are presently being written up for publication and for dissemination to interested groups on the Georgia Tech campus.

Conclusions: The major conclusion from the completed research is that the channeltron electron multiplier will provide a suitable detector with a 100% detection efficiency for all projectiles which are to be used in the primary research program.

The major objective of the program is being investigated at the present time.

Students:

Mr. R. L. Fitzwilson (Ph.D.)

Dr. N. Fox (Post Doctoral Student)

11. Microwave Absorption by Gases – T. L. Weatherly and J. Q. Williams

The microwave absorptions studied are associated primarily with changes in molecular rotation energies. However, the absorption frequencies are influenced slightly by nuclear electric quadrupole moments and, in the case of an applied electric field, by the molecular dipole moment. The purpose of these studies is to test the theory for quadrupole interactions in molecules containing two and three identical quadrupolar nuclei and to measure the quadrupole coupling constants and electric dipole moments of such molecules.

The Stark effect studies on the molecules $CHCl_3$ and $CFCl_3$ are now complete. The theory for the electric quadrupole interactions plus Stark effect developed by Dr. C. R. Nave was completely adequate for these molecules. The electric dipole moment of $CHCl_3$ was found to be 1.04 ± 0.02 debye and that for $CFCl_3$ was found to be 0.46 ± 0.02 debye. This work was the subject of Mr. P. B. Reinhart's Ph.D dissertation. Mr. Reinhart will receive his Ph.D. degree in June. The results of Dr. Nave's work have been published in the article listed below.

The investigation of electric quadrupole interactions in molecules containing two identical quadrupolar nuclei is continuing. Calculations have been made for several molecules and in all cases the 2nd order effects, which are of greatest interest, are small. At present

the molecule CH_2Br_2 is being studied. This molecule has a very rich spectrum which has not been analyzed previously.

The experimental work on resonant cavity absorption cells is continuing. A K-band cell of this type will be tested soon, and we hope to have more to report on this work in the near future.

Graduate Students:

P. B. Reinhart - Will receive his Ph.D. in June, 1969.

Foch Tsai - Candidate for Ph.D.

William A. Little - Candidate for Ph.D.

Publications: "Quadrupole Hyperfine Structure in the Microwave Spectra of Phosphorous Trichloride and Phosphoryl Chloride," C. R. Nave, T. L. Weatherly and Quitman Williams, J. Chem. Phys. 49, 1413 (1968).

12. Control of Systems with Boundedness Constraints — R. P. Webb

Objectives: The objectives of this research are the development of practical techniques for the optimization of control systems which are constrained to operate with the system variables between prescribed bounds. The emphasis is placed on developing control algorithms resulting in near optimal control performance.

Description of Work Performed: The majority of the effort devoted to this project has been in connection with two Ph.D. thesis problems. One of these problems has been completed while the second is continuing. Also, two additional thesis problems have been generated by this effort. These are currently being worked on by students not supported by this project.

The thesis completed considered the problem of controlling a

system to a fixed point when magnitude constraints are imposed on both the system state and input variables. The approach taken was to compute the regions of state space from which the target could not be reached and then optimize the system trajectory over a finite interval to avoid these regions.

The thesis now underway considers the problem of tracking a moving target set with bounds placed on both the state and input variables. The Kuhn-Tucker theorem is being employed to determine the optimal control strategy.

Results and Conclusions: A method for solution of the discrete regulator problem with boundedness constraints on both state and control variables has been achieved. The method has been used successfully on several sample problems. The method results in an algorithm determined in terms of system dynamics and bounds which is digitally implemented.

A method for the solution of the discrete tracking problem with boundedness constraints is being developed. This problem is more difficult due to the fact that the boundedness constraints become time variable functions of the trajectory being tracked. A technique based on the Kuhn-Tucker theorem is being investigated and several examples have been worked.

Graduate Students:

J. S. Boland, III (Ph.D.)

P. W. Sowa (Ph.D.)

Publications: "On the Optimal Control of Discrete Systems with Bounded State Variables and Bounded Control Variables," Ph.D. dissertation by Joseph S. Boland III, Georgia Institute of Technology, August 1968.

Paper Presentations: "On the Optimal Control of Discrete Systems with Bounded State Variables and Bounded Control Variables" by J. S. Boland, R. P. Webb presented at the "Second Hawaii International Conference on System Sciences," January 1969.

13. Studies in Nitrene Chemistry – L. H. Zalkow, J. A. Bertrand and C. L. Liotta

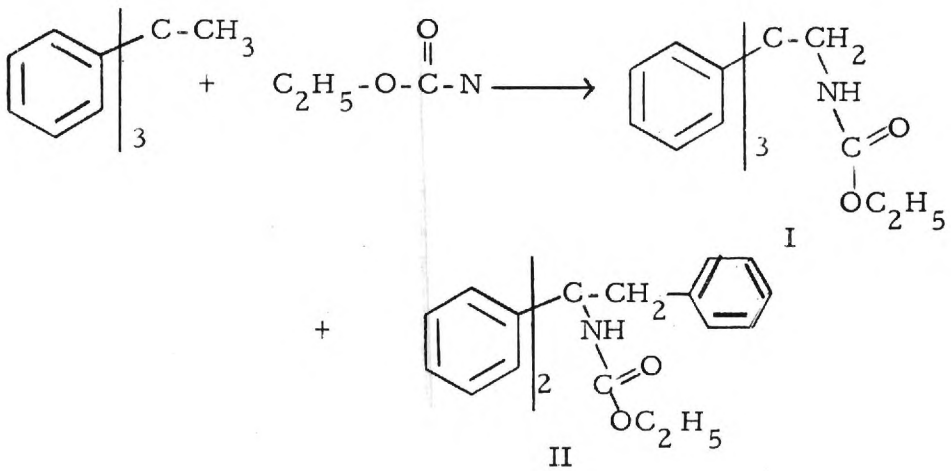
Objectives: A study of the properties and reactions of nitrene is proposed. Nitrenes are high energy electron-deficient nitrogen species; the parent compound, NH, has been observed to be a component of the sun, of comets, and of Jupiter; nitrenes have also been postulated as intermediates in a number of organic reactions. This study will include investigation of the electronic structure of nitrenes and investigations of the reactions of nitrenes with organic and inorganic substances. Results of this study should improve our understanding of why these species exist in space, how they may interact with man and spacecraft, and how they may be utilized in space exploration.

Description of Work and Results:

The Electronic Nature of Carbethoxynitrene

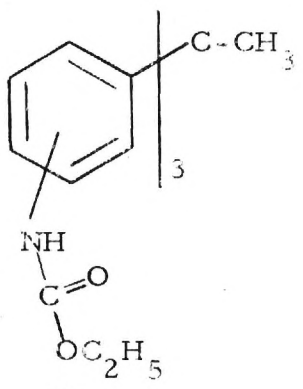
The following reactions are presently being investigated:

(a)

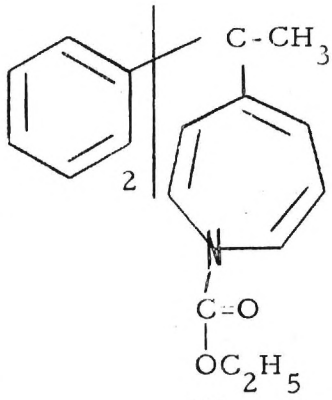


The ratio of the product I and II should be a sensitive measure of the multyplicity of the reacting nitrene - product I is expected from reaction of singlet nitrene while product II is expected from reaction of triplet

nitrene. Our investigation, to date, reveals that more than two products are formed. These could arise from attack of the electron deficient nitrogen species on the aromatic rings to form the following:



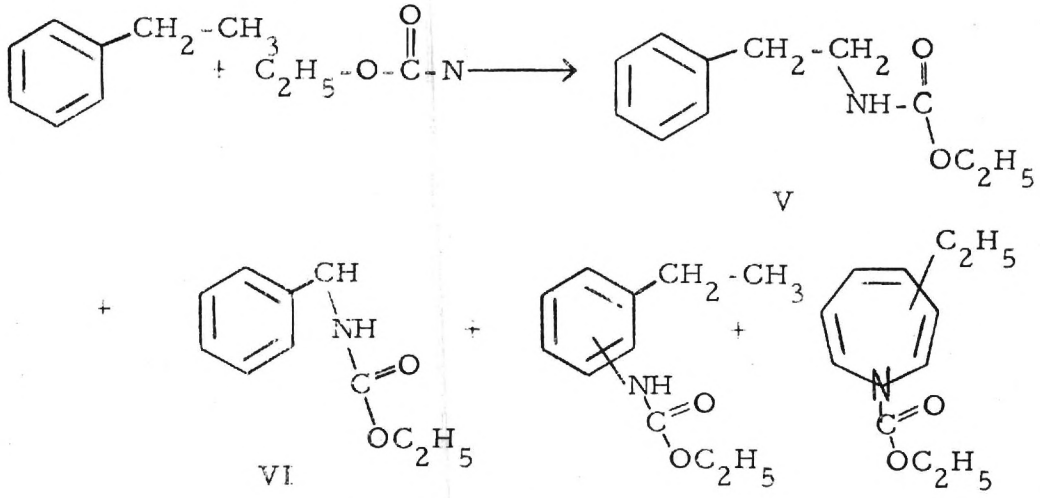
III



IV

These products are presently being investigated.

(b)



V

VI

From the ratio of products V and VI, information concerning the electriphelic character of carbethoxynitrene may be obtained. These data will be compared to similar reactions involving chlorine and bromine radicals.

Complexes of Aromatic Azides with Transition Metals:

Attempts have been made to prepare complexes of aromatic azides with cobalt, nickel, and copper compounds. The aromatic azides are stable in the presence of these metal ions and there is evidence from spectral measurements on solutions that complexes are formed with copper (II). No solid complexes have been isolated.

THE REACTION OF BENZENESULFONYL AZIDE WITH cis-endo AND cis-exo NORBORNENE-5,6-DICARBOXYLIC ACID ANHYDRIDES AND METHYL ESTERS. THE FORMATION OF endo AZIRIDINES FROM exo TRIZAOLINES.

Benzenesulfonyl azide reacts with cis-endo and cis-exo norbornene-5,6-dicarboxylic anhydrides and with the corresponding cis-exo-dimethyl ester in refluxing carbon tetrachloride to give predominantly endo aziridines. Under identical conditions the cis-endo dimethyl ester gives exclusively the exo aziridine and under photolytic conditions the cis-exo and cis-endo anhydrides and dimethyl esters give almost exclusively exo aziridines. At room temperature, the cis-exo dimethyl ester gives predominantly the exo aziridine, and p-methoxybenzenesulfonyl azide reacts with the endo-anhydride Ia in refluxing carbon tetrachloride to give an even greater ratio of the endo aziridine. The exo-1,2,3-Δ^2-trizaoline prepared from the exo anhydride and phenyl azide, on pyrolysis in decalin, gives an almost 1:1 ratio of the exo and endo aziridine.

A mechanism has been proposed to account for the above observations which invclves the conversion of exo-1,2,3-Δ^2-triazolines to endo aziridines via a 3-diazomethylcyclopentane-2-carboxaldehydeimine intermediate.

Conclusions: In the case of carbethoxynitrene, both the singlet and the triplet nitrene react with the organic substrate.

In the reaction of benzenesulfonyl azide with bicyclic alkenes, the thermal reaction does not involve a nitrene while the photolytic reaction does involve a nitrene. The stereo-chemistry of attack of the nitrene is almost exclusively exo.

Graduate Students:

R. H. Hill	(Ph.D.)
C. Shen	(Ph.D.)
C. Kirkwood	(Ph.D.)

Publications: "The Reaction of Benzenesulfonyl Azide with cis-endo and cis-exo Norbornene-5,6-dicarboxylic Acid Anhydrides and Methyl Esters," R. L. Hale and L. H. Zalkow, Tetrahedron, in the press.

III. CONCLUSIONS

The NASA Multidisciplinary Grant NGL 11-002-018 continues to stimulate research on the campus and its effectiveness is clearly demonstrated by the number of publications (10), acceptances (3), submissions (1) and presentations (12) during the six month period, September 15, 1968 to March 14, 1969.

Through the grant graduate students are engaged in quality research activities and students in the following categories received financial support from the grant: Undergraduates - 3, M.S. - 7, Ph.D - 19, and Post Doctorals - 3.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT

NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

ANNUAL REPORT

March 15, 1970 to September 14, 1970

Report Prepared by

A. L. Ducoffe, Chairman

Georgia Tech Space Sciences Technology Board

October 15, 1970

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

Office of
The Vice President for
Academic Affairs

October 15, 1970

Dr. Francis B. Smith
Assistant Administrator for
University Affairs
National Aeronautics and Space
Administration
Washington, D. C. 20546

SUBJECT: Annual Report
March 15, 1970 to September 14, 1970
Multidisciplinary Research Grant NGL 11-002-018

Dear Dr. Smith:

The Georgia Institute of Technology Space Sciences and Technology Board is pleased to submit herewith thirty (30) copies of an annual report for Multidisciplinary Research Grant NGL 11-002-018.

We shall be pleased to provide any additional information that you find necessary.

Sincerely yours,

V. Crawford
Vice President for
Academic Affairs

VC/mjs

Enclosures

cc: Mr. H. L. Baker
Members of the Space Sciences and Technology Board

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ANNUAL REPORT

March 15, 1970 to September 14, 1970

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

I. SUMMARY

The National Aeronautics and Space Administration granted the Georgia Institute of Technology $600,000 on June 15, 1964, $300,000 on June 15, 1965, $300,000 on March 15, 1966, $300,000 on March 15, 1967, and $100,000 on March 15, 1968 for the support over six years and nine months of basic scientific research entitled "Multidisciplinary Research in the Space Sciences and Technology."

The grant funds have been used to support an expansion of multidisciplinary research programs in materials and materials processing, transport phenomena, energy conversion, systems, and nuclear processes.

The grant has been administered by the Space Sciences and Technology Board established at the Georgia Institute of Technology. The Chairman of the Board is Dr. A. L. Ducoffe, Director of the School of Aerospace Engineering. The other Board members are H. F. Bauer, Engineering Mechanics; C. H. Braden, Physics; W. O. Carlson, Acting Dean of Engineering; J. W. Hooper, Electrical Engineering; R. H. Kasriel, Mathematics; P. Kelly, Social Sciences; H. A. McGee, Jr.,

Chemical Engineering; and W. M. Spicer, Director, School of Chemistry.

The last grant period runs from March 15, 1970 through March 14, 1971. The present document reports the research results obtained during the first six months of this period.

An indication of the research activity stimulated by the grant during this reporting period is the publication in recognized journals of 4 papers and the submission of 4 additional. Three papers have been read at scientific meetings. During the present grant period 2 Undergraduate students, 1 Masters student, 10 Ph.D. students and 1 Post Doctoral participated in the research effort.

II. RESEARCH RESULTS

1. Complex Metal Hydrides. High I_{sp} Fuel Components - E. C. Ashby

During this report period, efforts have been directed towards the preparation of complex metal hydrides of the type $M_nM'_{n'}H_{n+2n'}$, where M is an alkali metal or a cation such as NR_4^+, M' is a group II metal like Be, Mg, Zn, Cd, Hg and n or n' = 1, 2, 3. Using different combinations of the alkali metal and the group II metal it should be possible, in principle, to prepare a whole series of new hydrides. The first major breakthrough in this direction was made earlier in our laboratories with the successful preparation of $KMgH_3$, $NaMgH_3$ and $Na_2Mg_2H_5$. These compounds were prepared by the hydrogenolysis or pyrolysis of complexes of KH and NaH with $(s\text{-}C_4H_9)_2Mg$ in benzene.

$$KH + R_2Mg \rightarrow KMgR_2H \xrightarrow{H_2} KMgH_3 + 2\ RH \qquad (1)$$

Due to the unique solubility in benzene of $MM'R_2H$ compounds where R = s-butyl, the necessity of hydrogenolysis in more basic solvents such as ether can be avoided. The competition between solvent and hydride ion for coordination sites in the expected product is thus eliminated; in addition, secondary butyl groups bonded to relatively electropositive metals are known to undergo hydrogenolysis under mild conditions.

It was decided to attempt first the preparation of trihydridomagnesiate complexes of lithium and NR_4^+, in order to complete the $NMgH_3$ series where M = Li, Na, K, NR_4^+.

When KH is added to a solution of $(s\text{-}C_4H_9)_2Mg$ in benzene, the KH dissolves giving the compound $KMg(s\text{-}C_4H_9)_2H$. Similarly, NaH dissolves in a benzene solution of $(s\text{-}C_4H_9)_2Mg$ to form $Na[(s\text{-}C_4H_9)_2Mg]_2H$. However, when LiH was added to a benzene solution of disecondary butylmagnesium, no dissolution of LiH took place even after several days at higher temperatures.

When to a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in benzene, trioctylpropyl ammonium bromide was added, a precipitate formed after overnight stirring producing a solution light orange to purple in color.

$$KMg(s\text{-}C_4H_9)_2H + N(C_8H_{17})_3(C_3H_7)Br \xrightarrow[\text{Benzene}]{25^\circ}$$

$$N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H + KBr\downarrow \qquad (2)$$

I

The precipitate was determined to be potassium bromide. The filtrate upon analysis showed potassium and bromide to be absent. Upon removal of solvent an oily orange product resulted. This oil (I) reacted with water slowly and incompletely and quantitative hydrolysis even with concentrated hydrochloric acid at 80° could not be achieved. The yield of active hydrogen and butane was about 60% of the theoretically required value.

Although the direct reaction of KH with $(s\text{-}C_4H_9)_2Mg$ did not proceed in tetrahydrofuran, the compound $KMg(s\text{-}C_4H_9)_2H$ prepared from benzene dissolved readily in THF. The solution was not very stable at room temperature. At low temperatures, however, it was stable up to five days and no THF cleavage was observed.

When a tetrahydrofuran solution of $KMg(s\text{-}C_4H_9)_2H$ was added to trioctylpropyl ammonium bromide in THF, quantitative precipitation of KBr took place and the filtrate upon solvent removal produced the oily orange $N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H$ (I). Analysis of the THF solution of this compound was not quite as difficult as that of the benzene solution. The Mg:Butyl:H ratios were found to be 1:1.90:0.92. The infrared spectrum of the neat material was similar to that of $KMg(s\text{-}C_4H_9)_2H$ with the characteristic broad absorption envelope between 1300 and 600 cm^{-1} (ν Mg-H).

A solution of (I) in benzene when hydrogenolyzed under 3000 psi of hydrogen at 60-70° overnight produced a white gelatinous precipitate. Analysis showed about 30% magnesium to be present in solution. The dried solid gave the following analysis: Mg:H:Butyl = 1:2.7:0.2.

$$N(C_8H_{17})_3(C_3H_7)Mg(s\text{-}C_4H_9)_2H \xrightarrow[H_2,\ 3000\ psi]{Benzene,\ 60\text{-}70^\circ} \underset{(II)}{N(C_8H_{17})_3(C_3H_7)MgH_3}\downarrow \quad (3)$$

Further characterization of (II) by X-ray powder pattern and DTA-TGA analysis is in progress.

When a freshly prepared solution of $KMg(s\text{-}C_4H_9)_2H$ in tetrahydrofuran was added to an equivalent amount of lithium bromide in THF, KBr precipitated quantitatively after overnight stirring.

$$KMg(s\text{-}C_4H_9)_2H + LiBr \xrightarrow{THF,\ 25^\circ} \underset{(III)}{LiMg(s\text{-}C_4H_9)_2H} + KBr\downarrow \quad (4)$$

Analysis of the clear filtrate gave the following ratios: Li:Mg:Butyl:H = 1:1.12:2.04:0.93. Upon solvent removal under vacuum, an orange viscous material resulted. The infrared spectrum of this product was identical with the analogous potassium and tetraalkylammonium compounds. The THF solutions of (III) at room temperature are apparemtly more stable than those of the potassium compound.

Attempts to hydrogenolyze a THF solution of (III) have so far yielded inconclusive results. The mixture resulting from hydrogenolysis at room temperature under 3000 psi hydrogen produced a very small amount of a grey solid with negligible active hydrogen content. The supernatant solution was found to retain its original composition. Efforts are being continued to effect the hydrogenolysis of (III) under a variety of experimental conditions. With the right coice of temperature and solvent it would hopefully be possible to hydrogenolyze (III) to give $LiMgH_3$.

The fact that a tetrahydrofuran solution of $KMg(s\text{-}C_4H_9)_2H$ is stable for several days at low temperature opens up possibilities for the study of a large number of reactions in solution, such as chemical reductions with $LiAlH_4$, AlH_3, B_2H_6 to give possibly $KMgH_3$, $KMg(AlH_4)_3$ and $KMg(BH_4)_3$ respectively. Reactions of $KMg(s\text{-}C_4H_9)_2H$ with THF-soluble metal halides could give a variety of $MMg(s\text{-}C_4H_9)_2H$ type of intermediates which upon hydrogenolysis might be able to produce new and unusual $M(MgH_3)_n$ type of complex hydrides (n = 1, 2, 3 depending upon the metal M). Studies to explore these possibilities are currently in progress.

Significant Results: Preparation of R_4NMgH_3 where R_4N = trioctyl-n-propylammonium and precursors to $LiMgH_3$.

Publications:

(1) J. Dilts and E. C. Ashby, "Composition of Complex Metal Hydrides in Solution. I. Tertiary Amines," Inorg. Chem., 9, 855 (1970).

(2) S. Srivastava and E. C. Ashby, "Reaction of Aluminum Hydride with Diethylmagnesium in Tetrahydrofuran. Characterization of New Ethyl Substituted Hydridomagnesium Aluminum Hydrides," Inorg. Chem., (in press).

Graduate Students: One Postdoctoral student.

2. Vibration and Stability of Distensible Fluid Lines Carrying a Pulsating Incompressible Liquid - H. F. Bauer

Objectives of the Research:

The feedline system of liquid-propelled space vehicles

exhibits, in the problem of interaction with the combustion and pump dynamics and the longitudinally elastic structure, an oscillatory behavior. The propagation of viscous liquids in such a cylindrical elastic conduit will be investigated.

Description of the Work Performed:

The pulsating flow of an incompressible, viscous liquid in an elastic pipeline of circular cross section is investigated. The equations of motion of the liquid and structure have been derived and are given by:

The continuity equation: (because of symmetry)

$$(1) \qquad \frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z} = 0$$

The Navier-Stokes equation:

$$(2) \qquad \frac{\partial u}{\partial t} + u\frac{\partial u}{\partial r} + w\frac{\partial u}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left\{\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} - \frac{u}{r^2} + \frac{\partial^2 u}{\partial z^2}\right\}$$

$$(3) \qquad \frac{\partial w}{\partial t} + u\frac{\partial w}{\partial r} + w\frac{\partial w}{\partial z} = g - \frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left\{\frac{\partial^2 w}{\partial r^2} + \frac{1}{r}\frac{\partial w}{\partial r} + \frac{\partial^2 w}{\partial z^2}\right\}$$

where ν is the kinematic viscosity of the liquid and ρ is the mass density. If the pipeline has a wall thickness $\bar{h}$ and a diameter 2a, the behavior of the elastic cylindrical pipe may be approximately described by Donnell's Equations:

$$(4) \qquad \frac{\bar{\nu}}{a}\frac{\partial \bar{w}}{\partial z} + \frac{\bar{u}}{a^2} + \frac{\bar{h}^2}{12}\nabla^4\bar{u} + \frac{(1-\bar{\nu}^2)\bar{\rho}}{E}\frac{\partial^2 \bar{u}}{\partial t^2} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\left\{p\Big|_{r=a} - 2\mu\frac{\partial u}{\partial r}\Big|_{r=a}\right\}$$

$$(5) \qquad \frac{\partial^2 \bar{w}}{\partial z^2} + \frac{\bar{\nu}}{a}\frac{\partial \bar{u}}{\partial z} - \frac{(1-\bar{\nu}^2)}{E}\bar{\rho}\frac{\partial^2 \bar{w}}{\partial t^2} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\mu\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right)\Big|_{r=a}$$

where $\bar{\rho}$ is the mass density of the shell, $\bar{\nu}$ is Poisson's ratio, $\bar{u}$ the radial and $\bar{w}$ the longitudinal displacement of the shell. E is Young's modulus of elasticity, $\nabla^2 \equiv \partial^2/\partial z^2$ (because of the symmetry), and μ is the dynamic viscosity of the liquid. The equations of motion of liquid and pipeline wall are coupled by the conditions

$$(6) \qquad u = \frac{\partial \bar{u}}{\partial t} \qquad w = \frac{\partial \bar{w}}{\partial t} \qquad \text{at the wall, } r = a$$

For the solution of this hydroelastic problem, i.e. the simultaneous treatment of the equations (1) through (6), the liquid equations (2) and (3) have to be linearized. We consider a pipeline of infinite length and neglect gravity. Representing pressure and velocity as

$$(7) \qquad p = Pe^{i\omega(t-z/c)}$$

$$(8) \qquad u = U(r)e^{i\omega(t-z/c)}$$

$$(9) \qquad w = W(r)e^{i\omega(t-z/c)}$$

where ω is the circular frequency and c the speed of propagation, yields

$$(10) \qquad U' + \frac{1}{r} U = \frac{i\omega W}{c}$$

$$(11) \qquad U'' + \frac{1}{r} U' + (k^2 - 1/r^2)\, U = 0 \qquad \left(k^2 = \frac{i^3\omega}{\nu} - \frac{\omega^2}{c^2}\right)$$

$$(12) \qquad W'' + \frac{1}{r} W' + k^2 W = - \frac{i\omega}{\rho c \nu} P_o$$

which are for $\omega^2 c^2 \ll 1$ satisfied by

(13) $$W(r) = AJ_o(kr) - \frac{i\omega}{\rho c \nu k^2} P_o$$

and

(14) $$U(r) = \frac{i\omega A}{ck} J_1(kr) + \frac{\omega^2 P_o r}{2\rho\nu c^2 k^2}$$

A is an unknown integration constant. The elastic wall equations are

(15) $$\bar{u} = \bar{U} e^{i\omega(t-z/c)}$$

(16) $$\bar{w} = \bar{W} e^{i\omega(t-z/c)}$$

The resulting expressions are

(17) $$\bar{U}\left(\frac{1}{a^2} - \frac{(1-\bar{\nu})}{E}\bar{\rho}\omega^2\right) - \frac{\nu i\omega}{ac}\bar{W} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\left\{P_o - 2\mu\left[\frac{i\omega A}{c} J_1'(ka) + \frac{\omega^2 P_o}{2\rho c^2 \nu h^2}\right]\right\}$$

(18) $$-\frac{\bar{\nu} i\omega}{ac}\bar{U} + \bar{W}\left[\frac{(1-\bar{\nu}^2)\bar{\rho}\omega^2}{E} - \frac{\omega^2}{c^2}\right] = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\mu\left\{i\omega\left[\frac{i\omega A}{ck} J_1(ka) + \frac{a\omega^2 P_o}{2\rho c^2 \nu k^2}\right] + AkJ_o'(ka)\right\}$$

With the boundary conditions (6) one obtains two additional equations

(19) $$\frac{i\omega A}{ck} J_1(ka) + \frac{\omega^2 a P_o}{2\rho\nu k^2 c^2} = i\omega\bar{U}$$

(20) $$aJ_o(ka) - \frac{i\omega P_o}{\rho\nu ck^2} = i\omega\bar{W}$$

which together with (17) and (18) represent four equations for the determination of the unknowns. Introducing these into the equations (15), (16) and (7) through (9) gives the behavior of such a pulsating system.

Results:

The mathematical solution has been found for a simple pulsating system. The speed of propagation is obtained by setting the coefficient determinant obtained from equations (17) and (18) equal to zero. Thus the ratio A/P_o, $\bar{U}/P_o$ and $\bar{W}/P_o$ may be obtained from the above equations. In the next phase the arbitrary pulsating pressure gradient superimposed on a uniform flow will be treated. Additional mathematical analysis relative to the project, recently submitted by Mr. S. C. Chang and performed primarily by him, will be incorporated in the final report on this project.

Publications:

None.

Graduate Students: One Ph.D. student.

3. A Study of Helicopter Blade Slap Noise - R. B. Gray

Research Performed and Results Obtained:

The interaction under certain flight conditions of a helicopter blade with the vortex field shed from preceeding blades produces a loud repetitive noise. Other studies have shown that a realistic mathematical model of the vortex structure is required for analysis of the noise generating mechanism. Such a model is not presently available. The objective of this grant is to explore several methods of measuring the flow field associated with vortex systems. At present, the hot-wire anemometer is being used to study the flow field of vortex rings generated in air.

To date, velocity surveys across a ring diameter have

been made at the vortex generator exit and at a station twelve inches from the exit. Both the axial component and the total velocity magnitude have been measured. Although there is some scatter in the data, the results appear reasonable. However, a comparison with vortex ring models available in the literature is not good. In continuing the study, stronger rings will be generated to reduce the scatter in the data. An attempt will also be made to determine the vorticity distribution in the ring from the velocity measurements.

Publications:

(1) "Hot-Wire Velocity Surveys with Pressure-Velocity Correlation of Air Vortex Rings", John F. Betsill, Jr. Georgia Institute of Technology, School of Aerospace Engineering, Masters' Special Problem. September 4, 1970.

Graduate Students: One M. S. student.

4. Application of Mass Spectrometric and Cryogenic Methods to the Analysis and Synthesis of Highly Unstable Boron Compounds - H. A. McGhee, Jr.

As part of a multi-faceted theoretical and experimental research program in High Energy Chemistry, we have been concerned with the synthesis and chemistry of highly unstable and reactive compounds of boron. A scientifically particularly interesting and also important from an applications perspective class of compounds are ethylene-like and acetylene-like compounds of boron and nitrogen.

Non-aromatic (non-"borazine type") boron-nitrogen-hydrogen compounds such as NH_2-BH_2 and NH=BH, and their halogen derivatives

are very unstable. Classical organic or inorganic synthetic methods usually fail because of their strong tendency to fast degradation and formation of unstable polymer products of undetermined composition.

A promising route has been developed in this laboratory[1] wherein borazine is discharged in a low pressure inductive plasma followed by a rapid quench of the intermediate product NH_2-BH_2 in a liquid nitrogen cooled mass spectrometric inlet system. Slow fractional low temperature vacuum distillation directly into the ion source of the mass spectrometer led to the detection and identification of NH_2-BH_2. Also a direct mass spectrometric analysis of the gas mixture behind the plasma discharge indicated the existence of the compound. It was postulated that halogen derivatives such as NH_2BCl_2, NH=BCl, and flourine analogs also might exist as short life time intermediates. A similar way to get to those compounds would therefore be to discharge the corresponding 3 - halogeno borazines, however, the vapor pressures are too low for evaporation into the plasma-discharge because of their heteropolar character. Therefore, the alternative, but more difficult route was undertaken to primarily synthesize appropriate parent compounds as NH_3BCl_3 and NH_3BF_3 and decompose these unstable compounds in a one step process.

An apparatus has been designed whereby either the components NH_3 and BCl_3 or NH_3 and BF_3 can be discharged in a plasma directly in the mixing area or only one may be discharged with the second component introduced thereafter. The reaction products were analyzed by a Bendix time-of-flight mass spectrometer in order to determine the

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[1] C. T. Kwon and H. A. McGhee, Jr., Inorg. Chem. in press.

most favorable conditions (total pressure, residence time, composition ratio of the two initial compounds, and discharge current) for the yield of one particular compound as NH_2BCl_2. When the maximum peak height of NH_2BCl_2 (or the BHNF compound) occurred in the mass spectrum, the reaction mixture was trapped at liquid nitrogen temperature for further study. The total pressure was varied between 100 to 1000 microns of mercury. During the time when the mixture was trapped small amounts of the products were aspirated into the mass spectrometer for continuous analysis. This turned out to be very important because a change of the composition ratio had to be corrected immediately. Thereafter the liquid nitrogen was exchanged by 2 - methylpentane, at its melting point of -159°C. This refrigerant was then slowly heated up to room temperature within two to four hours and the sequentially vaporized products were analyzed with the Bendix mass spectrometer.

Roughly about one half of the reactants formed a white solid product directly at the point where they were mixed together. It was slowly soluble in water. No further analytical investigations were conducted on this product.

The gaseous part was analyzed mass spectrometrically. In general the spectra were similar with or without discharge of the reaction mixture. Therefore, if not specified otherwise, the following description applies to both cases. As mentioned above, the ratio of composition of NH_3 and BCl_3 was the most important factor for the formation of the final products. Depending on this ratio three

different products were obtained.

At excess amounts of ammonia, the only significant mass peaks belonged to ammonia (NH_3, NH_2, NH, N, N_2, H_2). Consequently a discharge of this reaction mixture gave N_2 and H_2 as decomposition products of NH_3. With excess amounts of BCl_3, only mass peaks of BCl_3 and of nitrogen were observed. HCl and N_2 are decomposition products of the unstable intermediate compound NH_3BCl_3 or its polymeric products. In the first case, HCl was not obtained because it reacts with excess NH_3 to form solid NH_4Cl.

Within a very small range of equal NH_3/BCl_3 composition, suddenly new peaks with the mass numbers 96-101 and 60-64 appeared while the mass intensities of BCl_3, BCl_2, BCl decreased. At a definite composition ratio only these new mass peaks were observed (together with HCl, Cl) while the BCl_3 peaks nearly decreased to zero. It can easily be proven that the peaks at 96-101 only belong to the compound NH_2BCl_2 because boron and chlorine are both isotopic and the natural abundances of these isotopes (B11: 80%, B10: 20%, Cl35: 75%, Cl37: 25%) are nearly ideal for a statistical analysis of the experimental mass intensity distribution. Table 1 shows the theoretical peak heights of NH_2BCl_2 of the mass numbers 96 to 101 in comparison to the experimental results.

Table 1

Theoretical and experimental mass intensity distribution for the compound NH_2BCl_2.

mass	96	97	98	99	100	101
I_{theo}	25	100	16.6	66.7	2.8	11.1
I_{exp}	26.9	100	18.7	65.6	2.5	13.1

The experimental values are averages of 11 independent measurements. The electron voltage at the ion source was in all cases 70 volts.

The close agreement between theoretical and experimental data leaves no doubt, that only NH_2BCl_2 contributes to above mass intensity distribution.

The peaks at the mass numbers 60-64 were analyzed in the same way and turned out to be superpositions of mainly NH_2BCl with small amounts of NHBCl. These are obviously fragmentation products. When the amount of NH_3 was increased, the NH_2BCl_2 peaks were dimished at once. When the amount of BCl_3 was marginally increased one could observe NH_2BCl_2, NHBCl together with BCl_3, BCl_2, BCl, but at further increase of BCl_3 the boron-nitrogen compound disappeared in the spectrum. This implies that both, excess NH_3 and BCl_3 are reacting with NH_2BCl_2 towards decomposition and/or polymerization. These results help to clarify why NH_2BCl_2 has never been observed before.

Current research here is concerned with efforts to quench-stablize NH_2BCl_2 at cryogenic temperatures. Our unique cryogenic mass spectrometric techniques will be indispensible for this investigation.

5. Energy Conversion in Reactive Collisions - T. Moran

Inelastic energy losses in the collisions of O^+ and O_2^+ ions with neutral molecules have been studied in a beam apparatus

designed to direct mass-analyzed low energy ion beams onto taget molecules and scan the mass, energy and angular distributions of charged reaction products. Elastic collisions are found to predominate in the forward scattering events, however inelastic collisions become important at large scattering angles. Maxima in the inelastically scattered ion intensities are displaced from the centroids of the elastic peaks by amounts corresponding to known vibrational energy spacings in the respective diatomic species. Vibrational transition probabilities obtained from the inelastic data show multiquantum transitions to be more important as the reactant ion kinetic energy is increased from 10 to 20eV. For a given relative energy of approach, it is found that higher vibrational transitions predominate at larger scattering angles. The velocity dependences of these transitions are in reasonable accord with calculations that employ a semiclassical impact parameter treatment to estimate collisional energy transfer and time dependent wavefunctions to evaluate vibrational transition probabilities for a forced harmonic oscillator model.

A statistical phase space model of chemical reactions has been developed and applied to the above inelastic energy loss process and it is found inferior to the forced quantum oscillator model; however, further examination of the statistical model shows that it can be extremely useful in describing chemical rearrangement channels of reaction. This statistical model has been applied to molecular and dissociative charge transfer reactions of He^+, Ne^+, Ar^+ and Kr^+ with neutral molecules in the 0.05 to 200eV energy range. Comparison between calculated and experimental cross sections for the molecular charge transfer channels have indicated an incomplete mixing of

statistically available N_2^+ product ion electronic states, however the cross sections computed for endoergic dissociative channels of reaction are in good agreement with experiment. Calculated product ion vibrational distributions are found to be in accord with those obtained from product N_2^+ kinetic energies and with vibrational distributions obtained from spontaneous radiative transitions of electronically excited N_2^+ ions produced in the respective chemical interactions.

The statistical model of energy conversion processes has been applied to experimental results obtained in the ion beam lab at Tech and recent results from the Aerospace Research Laboratories of Wright-Patterson AFB. The in-line high collection efficiency configuration of a tandem mass spectrometric beam apparatus at the latter location is unique and their data is supplementary to the results obtained with the beam apparatus at Georgia Tech. Cross sections for the collision induced dissociation of excited O_2^+ and NO^+ ions computed using the statistical model is in surprising agreement with existing experimental data. The variation of the calculated cross sections with both ion internal energy and ion kinetic energy are in good agreement with experiment. The statistical theoretical model of reaction thus appears to be a very effective tool in its predictive properties, in particular the involvement of vibrational and electronic excitation energy in the high energy dissociative reactions.

Publications:

(1) "H_3^+ Vibrational Frequencies from Ion Impact Spectroscopy,"

F. Petty and T. F. Moran, Chem. Phys. Lett. 5, 64 (1970).

(2) "Vibrational Excitation in Collisions Involving Oxygen Ion Beams," P. C. Cosby and T. F. Moran, J. Chem. Phys. 52, 6157 (1970).

(3) "Application of the Statistical Phase Space Theory to the Reactions of Rare Gas Ions with Nitrogen Molecules," D. C. Fullerton and T. F. Moran, Submitted to J. Chem. Phys.

(4) "Statistical Phase Space Model of the Collision-Induced Dissociation of Excited O_2^+ and NO^+ Ions," T. F. Moran and D. C. Fullerton, Submitted to J. Chem. Phys.

Graduate Students: Two Ph.D. students.

6. Atomic and Magnetic Ordering in Transition Metal Alloys - S. Sponner

Summary of Progress:

Neutron diffraction studies of the effects of atomic ordering on the atomic magnetic moments using the polarized neutron scattering technique have been continued at Oak Ridge National Laboratory with the cooperation of J. W. Cable of the Solid State Division. After preparing a draft of a research paper based on neutron data taken last fall, it was concluded that the findings were of sufficient importance that the existing experimental uncertainties should be removed before final publication. In review, the conclusions are as follows:

1. Changes in the atomic magnetic moments of iron in iron-50% cobalt alloys cannot be explained by short-range order effects.

2. A large negatively polarized non-local spin density is present in the FeIo in both the ordered and disorder state.
3. A spin density transfer of a non-localized nature appears to reduce the constituant moments in the alloy where the negative spin polarization may be found preferentially at the iron site.
4. The long-range order changes appear to be chiefly responsible for iron moment changes, possibly through the effects of an order induced Brillouin zone boundary pertubation of the 3d-4s bands.

A draft copy of these results was brought to the attention of Solid State physics theorists at the recent Sagamore conference on Magnetic Electron Density at Grenoble, France, by Dr. R. A. Young. The keen interest in the findings has made analysis and publication of our new neutron scattering results an immediate objective in the program.

Metallurgical studies of iron-cobalt alloys have also continued with the objective of elucidating the engineering factors in iron-cobalt alloy development and the production of mere suitable alloy samples for diffraction analysis. The limitation to grain growth appears already to be related to carbide pinning of grain boundaries. For some time it has been held that interstitial impurities have been responsible for imbrittling the iron-cobalt alloys. The role of vanadium additions in commercial alloys appears, from our studies, to act as a carbon scavenger in the iron-cobalt solid solutions. The behavior carbon in iron cobalt solutions is

under investigation with vanadium carbide formation a principle objective.

Publications: None.

Graduate Students: Two Ph.D. students.

7. A New Technique for Detection of Infrared Radiation - A. L. Stanford

Objectives of the Research:

To investigate materials and fabrication techniques for utilizing the pyroelectric effect as a thermal detector.

Description of Work Performed:

Our inability to observe the pyroelectric effect in biological samples has prompted a return of studies to the more common ferroelectric materials.

The combination of thermal (beat sinking) and electrical (rise time) problems have limited the use of $BaTiO_3$ and GASH (quanadive aluminum sulfate hexahydrate) as an infrared detector, except when sources of radiation are relatively intense. Using gold-coated crystals of $BaTiO_3$, rise times as low as 0.5 msec have been observed by sacrificing detectivity. With rise times of about 30 msec, detectivities of about 15×10^6 $cm^{1/2}$ $watt/cps^{1/2}$ have been achieved. In our samples, this corresponds to noise equivalent power of approximately 1.3×10^{-8} $watt/cps^{1/2}$.

With the normal ferroelectric materials, including triglycene sulfate (TGS), it does not appear that pyroelectric detectors will compete successfully with quantum detectors in the infrared region. However, with high intensity sources like lasers, fast rise times in pyroelectric detectors might be utilized in mode studies, calibrating output

energy, and in numerous situations where a rugged, small detector can be placed in the beam.

Publications: None.

Graduate Students: None.

8. The Physical and Functional Aspects of Integrated-Circuit Technology - K. L. Su and D. C. Ray

Research Performed:

In the circuit phase, work has been centered around the extension of synthesis techniques to the use of the generalized positive-impedance converter (GPIC) in active RC networks. The GPIC is characterized by the chain matrix in which $A = \pm k_1$, $B = 0$, $C = 0$, and $D = \pm k_2 f(s)$; where k_1 and k_2 have the same algebraic sign. If port 2 is terminated in Z_L, then the impedance looking into port 1 is $\frac{k_1}{k_2} f(s) Z_L$. In particular, it has been found advantageous to investigate the case in which $f(s) = 1/s$.

A grounded minimum-capacitor synthesis technique for a qth order arbitrary open-circuit voltage transfer function of real rational functions in the complex variables utilizing only resistors and GPIC's has been developed. It has been shown that the technique can be made compatible with hybrid integrated-circuit technology.

The coefficient, selectivity, and natural-frequency sensitivities have been examined for the second-order open-circuit voltage transfer function and found to be small. An advantage in selectivity sensitivity has been noted over a certain INIC realization of the second-order open-circuit voltage transfer function.

The range of passive elements (resistors) has been examined for the case where K_1 and k_2 of the GPIC can take on any real value. It has been found that all resistors in the synthesis can be restricted to have values of 1 ohm if so desired. This serves as a good indicator of the potential control over the range of passive element values in the synthesis technique.

A grounded minimum-capacitor synthesis technique for a qth order arbitrary driving-point admittance which is a real rational function in the complex variables utilizing only resistors and GPIC's has been developed. The driving-point function is rendered in terms of an open-circuit voltage transfer function and is synthesized accordingly.

In the devices area, the effort can be broken down into two parts. The first part deals with a continuation of the previous work on thin-film active devices for operation at microwave frequencies. The second part was concerned with establishing the goals for a Ph.D. dissertation based on the work accomplished on this grant. The details of these two parts are as follows.

An extension of the measurement of the microwave conductivity of a specimen by eddy current loss techniques was developed which includes the important case of a semiconductor film deposited on an insulating substrate. The dissipated power in terms of the dimensions and physical properties of the film and substrate has been determined using the computer. The results are such that experimentation of simple dimensions is scheduled to be carried out on germanium deposited on calcium fluoride. The selection of the

the calcium fluoride was partially dictated by the availability of backup data at microwave frequencies and the fact that germanium has been deposited epitaxially on it. The experimentation is called for because the results suggest unpublished substrate effects in the films at microwave frequencies.

The dissertation work of a graduate student will involve an investigation, analytically and experimentally, of various transport phenomena in sputtered semiconducting films as a function of film thickness and structure. Both single-crystal and polycrystalline thin-film properties will be studied to determine the fundamental factors influencing the electrical behavior. Such factors as the treatment of band edges at the surface; symmetrical versus nonsymmetrical band edges; surface scattering - specular and diffuse; impurity scattering; thermal scattering; dislocation scattering; and a complete accounting of structure sensitive properties will be considered. The fabrication of the films and useful measurement structures are a direct outgrowth of the NASA research grant. It should be noted that the Schottky microwave diode fabricated using germanium on sapphire substrates did not possess the electrical characteristics that were desired due to certain problems in the fabrication procedures. The problems encountered have been solved and a useful thin-film device will be built in the near future to demonstrate this capability.

Paper Submitted for Publication:

(1) D. R. McElroy and K. L. Su, "Admittance Matrix Synthesis with Grounded RC Network Containing Nonideal Amplifiers," submitted to the IEEE Transactions on Circuit Theory.

Papers Presented at Scientific Meetings:

(1) K. L. Su, "An All-Purpose Impedance Converter Circuit," 1970 Chiao Tung Colloquium on Circuits and Systems; Hsinchu, Taiwan, China, August 25, 1970.

(2) K. L. Su, "Synthesis of RC Active Networks Using Positive-Impedance Converters," 1970 Kyoto International Conference on Circuit and System Theory, Kyoto, Japan, September 9, 1970.

Graduate Students: Three Ph.D. students.

9. Collisional De-excitation of Atomic Particles - E. W. Thomas

Objectives of the Research:

The experiments are designed to investigate the processes of formation and destruction of excited atoms at projectile energies of 5 to 30 keV. Work is presently concentrated on the metastable state of the hydrogen atom. Hydrogen atoms and ions are responsible for certain types of auroral phenomena. Results from the study of the metastable state may be readily extrapolated to other excited states by well established theoretical rules.

The research is to determine the cross sections for the formation of the metastable state of hydrogen as protons traverse targets of helium and nitrogen. Measurements are made as a function of the distance of closest approach between the colliding atoms. Experiments are also planned using metastable beams and monitoring their destruction.

Research Performed in the Current Period:

The objective of the present experiments is to study

charge transfer reactions that can be described as follows:

$$H^+ + X \rightarrow H(2s) + X^+$$

The ultimate objective is to study the angular scattering in such processes. As an initial step in the program it was decided to measure the total cross section (i.e. the cross section integrated over all scattering angles) for the case of a Helium target. It was intended to confirm the satisfactory operation of the experiment by comparing our data with previous measurements by other groups. The versatility of our apparatus permitted this measurement with great ease. Included in this phase of the work were total cross section measurements for targets of O_2 and N_2; no data on these cases is available in the literature. The cross sections for O_2 and N_2 rose with energy in the range 5 to 30 keV; cross section magnitudes were of the order 5×10^{-17} cm^2. This phase of our work is now complete and has been submitted for publication in "The Physical Review".

At the present time considerable progress has been made in the study of angular scattering in the charge transfer process. Attention is being directed at targets of He and N_2. It appears that the proportion of neutrals formed in the metastable state is a rather sensitive function of angle and energy; excited state fractions of 10% have been recorded at large angles. This is a most unexpected result. Apart from the intrinsic interest, this phenomenon could be used as a basis for design of metastable particle sources. At present there is no obvious explanation of these observations. Work in this

area continues.

Papers Submitted for Publication:

(1) A paper entitled "Formation of Metastable Hydrogen Atoms by Charge Transfer" has been submitted to "The Physical Review" for publication.

Paper Presented to Scientific Meetings:

(1) A paper entitled "Differential Cross Section for the Formation of Metastable Hydrogen by Charge Transfer" has been accepted for presentation at the Annual Meeting of the Division of Electron and Atomic Physics, American Physical Society (November, 1970, Seattle).

Students: One Ph.D. and two undergraduate students.

10. Studies in Nitrene Chemistry - L. H. Zalkow and C. L. Liotta

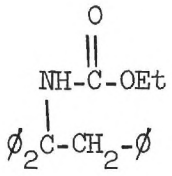
Objectives:

A study of the properties and reactions of nitrenes is proposed. Nitrenes are high energy electron-deficient nitrogen species; the parent compound, NH, has been observed to be a component of the sun, of comets, and of Jupiter; nitrenes have also been postulated as intermediates in a number of organic reactions. This study includes investigations of the electronic structure of nitrenes and investigations of the reactions of nitrenes with organic and inorganic substances. Results of this study should improve our understanding of why these species exist in space, how they may interact with man and spacecraft, and how they may be utilized in space exploration.

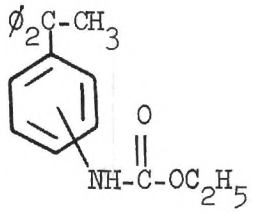
Description of Work and Results:

The Electronic Nature of Carbethoxynitrene

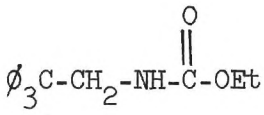
In order to distinguish between singlet and triplet carbethoxynitrene during time of reaction, a series of experiments were carried out in which carbethoxynitrene was allowed to react with 1,1,1-triphenylethane. The following products were isolated from the reaction mixture:



I



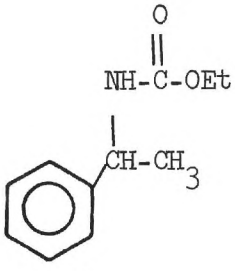
III



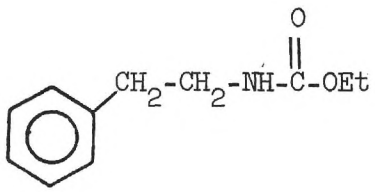
II

Product I is believed to arise from the interaction of 1,1,1-triphenylethane with triplet carbethoxynitrene, while II is believed to arise from singlet nitrene.

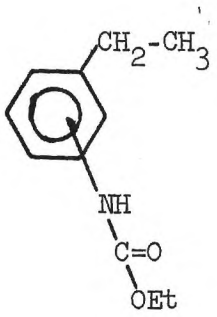
To obtain some information regarding the electrophilicity of carbethoxynitrene, a series of experiments was carried out in which carbethoxynitrene was allowed to react with ethylbenzene. The following products were obtained:



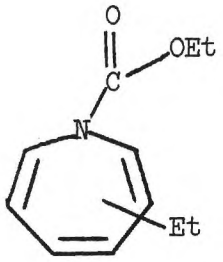
IV



V



VI



VII

The ratio of III to IV is an indication of the nucleophilicity of the attacking nitrene. This ratio was found to be much greater than one. The mechanism for the formation of VI may be explained in terms of singlet carbethoxynitrene. Compounds IV, V and the three isomeric structures of VI have been synthesized by alternate routes in order to prove the structures of the above products.

The Reaction of Various Azides with Bicyclic Olefins

The thermal reaction of methyl azidoformate and norbornene has been found to proceed via 1,3-dipolarcycloaddition yielding exo triazoline adduct. Thermal decomposition of the triazoline results in the loss of nitrogen and the formation of at least 5 products. The major products of the thermal decomposition in decalin were 3-carbomethoxy-3-azatricyclo(3.2.1.$0^{2,4}$ exo)-octane, and N-carbomethoxy-2-norbornimine. In addition, syn-2-norbornene-7-methyl carbamate, and 3-carbomethoxy-3-azatricyclo(3.2.1.$0^{2,3}$ endo)octane were isolated. The thermal decomposition of the triazoline adduct is considered to proceed by a multi-step mechanism. The first step is considered to involve heterolytic cleavage of the N_3-N_4 bond to give a zwitterion which may lead to products or rearrange via carbon-carbon bond

cleavage to give a diazoalkyl imine.

Benzenesulfonyl azide has been found to react with cis-endo and cis-exo bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride to give in both cases, predominantly the more hindered endo aziridine in addition to the exo aziridine in apparent violation of the "exo-addition rule." The stereo-chemistry of the aziridine rings was determined by nuclear magnetic resonance analysis and by conversion of the endo-aziridone-exo-anhydride to 2-endo-benzenesulfonamidobicyclo [2.2.1]heptane. The endo-aziridine-endo-anhydride has been previously converted into a lactone-N-benzenesulfonyl-lactam.

Benzenesulfonyl azide reacts with cis-endo and cis-exo-norbornene-5,6-dicarboxylic anhydrides and with the corresponding cis-exo-dimethyl ester in refluxing carbon tetrachloride to give predominantly endo aziridines. Under identical conditions the cis-endo dimethyl ester gives exclusively the exo aziridine and under photolytic conditions the cis-exo anhydrides and dimethyl esters give almost exclusively exo aziridines. At room temperature, the cis-exo dimethyl ester gives predominantly the exo aziridine, and p-methoxy-benzenesulfonyl azide reacts with the endo-anhydride Ia in refluxing carbon tetrachloride to give an even greater ratio of the endo aziridine. The exo-1,2,3-Δ^2-triazoline prepared from the exo anhydride and phenyl azide, on pyrolysis in decalin, gives an almost 1:1 ratio of the exo and endo aziridine.

A mechanism is proposed to account for the above observations which involves the conversion of exo-1,2,3-Δ^2-triazolines to endo aziridines via a 3-diazomethylcyclopentane-2-carboxaldehydeimine

intermediate.

Publications: None.

Graduate Students: Two Ph.D. students.

III. CONCLUSIONS

The NASA Multidisciplinary Grant NGL 11-002-018 continues to stimulate research on the campus and its effectiveness is demonstrated by the number of publications (4), submissions (4) and presentations (3) during the six month period, March 15, 1970 to September 14, 1970.

Through the grant graduate students are engaged in quality research activities and students in the following categories received financial support from the grant: Undergraduates - 2, M.S. - 1, Ph.D. - 10, and Post Doctorals - 1.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT

NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

FINAL REPORT

Report Prepared by

A. L. Ducoffe, Chairman

Georgia Tech Space Sciences Technology Board

April 15, 1971

GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia 30332

Office of
The Vice President for
Academic Affairs

April 15, 1971

Dr. Francis B. Smith
Assistant Administrator for
University Affairs
National Aeronautics and Space
Administration
Washington, D. C. 20546

SUBJECT: Final Report
Multidisciplinary Research Grant NGL 11-002-018

Dear Dr. Smith:

The Georgia Institute of Technology Space Sciences and Technology Board is pleased to submit herewith thirty (30) copies of the final report for Multidisciplinary Research Grant NGL 11-002-018.

We shall be pleased to provide any additional information that you find necessary.

Sincerely yours,

V. Crawford
Vice President for
Academic Affairs

VC/af

Enclosures

cc: Mr. H. L. Baker
Members of the Space Sciences and Technology Board

TABLE OF CONTENTS

FINAL REPORT

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH GRANT NGL 11-002-018

GEORGIA INSTITUTE OF TECHNOLOGY

I. SUMMARY

The National Aeronautics and Space Administration granted the Georgia Institute of Technology $600,000 on June 15, 1964, $300,000 on June 15, 1965, $300,000 on March 15, 1966, $300,000 on March 15, 1967, and $100,000 on March 15, 1968 for the support over six years and nine months of basic scientific research entitled "Multidisciplinary Research in the Space Sciences and Technology."

The grant funds have been used to support an expansion of multidisciplinary research programs in materials and materials processing, transport phenomena, energy conversion, systems, and nuclear processes.

The grant has been administered by the Space Sciences and Technology Board established at the Georgia Institute of Technology. The Chairman of the Board is Dr. A. L. Ducoffe, Director of the School of Aerospace Engineering. The other Board members are H. F. Bauer, Engineering Mechanics; C. H. Braden, Physics; W. O. Carlson, Mechanical Engineering; J. W. Hooper, Electrical Engineering; R. H. Kasriel, Mathematics; P. Kelly, Social Sciences; H. A. McGee, Jr., Chemical Engineering; and W. M. Spicer, Director, School of Chemistry.

The last grant period runs from March 15, 1970 through March 14, 1971. The present document reports the research results obtained during the last six months of this period.

An indication of the research activity stimulated by the grant during this reporting period is the publication in recognized journals of 5 papers and the submission of 3 additional. Two papers have been read at scientific meetings. During the present grant period 1 Masters student and 12 Ph.D. students participated in the research effort.

II. RESEARCH RESULTS

1. Vibration and Stability of Distensible Fluid Lines Carrying a Pulsating Incompressible Liquid - H. F. Bauer

Objectives of Research: The feedline system of liquid propelled space vehicles exhibits a peculiar interaction with the combustion and pump dynamics and the elastic structure. The problem occurs also in pressure fed systems, where no cavitation bubbles are present in the feedline. For the speed of propagation in the liquid of $c = \infty$, i.e., incompressible liquid, as it occurs in a pressure-fed system, the propagation of viscous liquid in an elastic cylindrical pipeline has been investigated.

Description of the Work Performed: The pulsating flow of an incompressible, viscous liquid in an elastic pipeline of circular cross section has been investigated for small displacements and velocities. The linearized basic equations are (because of symmetry) given by:

The equation of continuity:

$$\frac{\partial u}{\partial r} + \frac{u}{r} + \frac{\partial w}{\partial z} = 0 \tag{1}$$

The Navier-Stokes equations for incompressible flow:

$$\frac{\partial u}{\partial t} = + \nu\left[\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} - \frac{u}{r^2} + \frac{\partial^2 u}{\partial z^2}\right] \tag{2}$$

$$\frac{\partial w}{\partial t} = - \frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left[\frac{\partial^2 w}{\partial r^2} + \frac{1}{r}\frac{\partial w}{\partial r} + \frac{\partial^2 w}{\partial z^2}\right] \tag{3}$$

The behavior of the elastic cylindrical pipeline of infinite length is described by Donnell's shell equations:

$$\frac{\bar{\nu}}{a}\frac{\partial \bar{w}}{\partial z} + \frac{\bar{u}}{a^2} + \frac{h^2}{12}\frac{\partial^4 \bar{u}}{\partial z^4} + \frac{(1-\bar{\nu}^2)}{E}\bar{\rho}\frac{\partial^2 \bar{u}}{\partial t^2} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\left\{p\Big|_{r=a} - 2\mu\frac{\partial u}{\partial r}\Big|_{r=a}\right\} \tag{4}$$

$$\frac{\partial^2 \bar{w}}{\partial z^2} + \frac{\bar{\nu}}{a}\frac{\partial \bar{u}}{\partial z} - \frac{(1-\bar{\nu}^2)}{E}\rho\frac{\partial^2 \bar{w}}{\partial t^2} = \frac{(1-\bar{\nu}^2)}{E\bar{h}}\mu\left[\frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}\right]_{r=a} \tag{5}$$

The equations of motion of the liquid and elastic pipeline are coupled through the conditions

$$u = \frac{\partial \bar{u}}{\partial t} \quad \text{and} \quad w = \frac{\partial \bar{w}}{\partial t} \quad \text{at the wall } r=a. \tag{6}$$

Representing the pressure and velocities as

$$p = \frac{P_o}{2} z + \mathrm{Re}\left[\sum_{n=1}^{\infty} \left\{ P^*_{1n} \, e^{i\omega \, n(t-z/c_n)} + P_{2n} \, e^{i\omega \, n(t+z/c_n)} \right\} \right] \qquad (7)$$

with

$$P^*_{1n} = P_{1n} - i\bar{P}_{1n}$$

$$P^*_{2n} = P_{2n} - i\bar{P}_{2n}$$

where ω is the circular frequency and c_n is the speed of propagation, yields with:

$$u = \mathrm{Re}\left[\sum_{n=1}^{\infty} \left\{ U^*_{1n}(r) \, e^{i\omega \, n(t-z/c_n)} + U^*_{2n}(r) \, e^{i\omega \, n(t+z/c_n)} \right\} \right] \qquad (8)$$

and

$$w = \frac{W_o}{2} + \mathrm{Re}\left[\sum_{n=1}^{\infty} \left\{ W^*_{1n}(r) \, e^{i\omega \, n(t-z/c_n)} + W^*_{2n}(r) \, e^{i\omega \, n(t+z/c_n)} \right\} \right] \qquad (9)$$

the equations:

$$W_o'' + \frac{1}{r} W_o' = \frac{P_o}{\mu} \qquad (10)$$

and

$$U^{*\prime}_{\lambda n} + \frac{1}{r} U^{*}_{\lambda n} = \pm \frac{2n\omega W^{*}_{\lambda n}}{c_n} \tag{11}$$

$$U^{*\prime\prime}_{\lambda n} + \frac{1}{r} U^{*\prime}_{\lambda n} + \left(k_n^2 - \frac{1}{r^2}\right) U^{*}_{\lambda n} = 0 \tag{12}$$

$$W^{*\prime\prime}_{\lambda n} + \frac{1}{r} W^{*\prime}_{\lambda n} + k_n^2 W^{*}_{n\lambda} = \mp \frac{in\omega}{\mu c_n} P^{*}_{\lambda n} \tag{13}$$

where $k_n^2 = \frac{i^3\omega n}{\nu} - \frac{\omega^2 n^2}{c_n^2}$ and the upper sign belongs to $\lambda=1$, while the lower sign belongs to $\lambda=2$, the reflected waves. They are satisfied for $\omega^2 n^2 \ll c_n^2$ by

$$W_o(r) = \frac{P_o a^2}{4\mu}\left(1 - \frac{r^2}{a^2}\right) \qquad \text{(Poiseuille Flow)} \tag{14}$$

and

$$W^{*}_{\lambda n}(r) = A_{\lambda n} J_o(k_n r) \mp \frac{i\omega n}{\mu c_n k_n^2} P^{*}_{\lambda n} \tag{15}$$

$$U^{*}_{\lambda n}(r) = \frac{i\omega n}{c_n k_n} A_{\lambda n} J_1(k_n r) + \frac{\omega^2 n^2 r}{2\mu c_n^2 k_n^2} P^{*}_{\lambda n} \tag{16}$$

where $A_{\lambda n}$ are unknown integration constants. The elastic wall equations are with

$$\bar{u} = \frac{\bar{u}_o}{2} + \mathrm{Re}\Big[\sum_{n=1}^{\infty} \Big\{ \bar{U}^*_{1n}\, e^{i\omega\, n(t-z/c_n)} + \bar{U}^*_{2n}\, e^{i\omega\, n(t+z_o/c_n)} \Big\} \Big] \qquad (17)$$

$$\bar{w} = \mathrm{Re}\Big[\sum_{n=1}^{\infty} \Big\{ \bar{W}^*_{1n}\, e^{i\omega\, n(t-z/c_n)} + \bar{W}^*_{2n}\, e^{i\omega\, n(t+z_o/c_n)} \Big\} \Big] \qquad (18)$$

given by:

$$\Big(\bar{U}_o = \frac{(1-\bar{\nu}^2)\, a^2}{E\bar{h}}\, P_o \Big).$$

$$\bar{U}^*_{\lambda n}\Big[\frac{1}{a^2} - \frac{(1-\bar{\nu}^2)}{E}\, \rho\omega^2 n^2 \Big] - \frac{\nu i\omega n}{a c_n}\, \bar{W}^*_{\lambda n} = \frac{(1-\bar{\nu}^2)}{E\bar{h}} \Big[P^*_{n\lambda} - 2\mu \Big\{ \frac{i\omega n A_{\lambda n}}{c_n}\, J_1'(k_n a) + \frac{\omega^2 n^2 P^*_{\lambda n}}{2\mu c_n^2 k_n^2} \Big\} \Big] \qquad (19)$$

and

$$- \frac{i\omega n\bar{\nu}}{ac_n} \bar{U}^*_{\lambda n} + \bar{W}^*_{\lambda n}\left[\frac{(1-\bar{\nu}^2)\rho\omega^2}{E} - \frac{\omega^2 n^2}{c_n^2}\right] = \frac{(1-\nu^2)}{E\bar{h}} \mu\Big[i\omega n \Big\{\frac{i\omega n A_{\lambda n}}{c_n k_n} J_1(k_n a) \quad (20)$$

$$+ \frac{\omega^2 n^2 a^2 P^*_{\lambda n}}{2\mu c_n^2 k_n^2}\Big\} + A_{\lambda n} k_n J_o'(k_n a)\Big]$$

With the boundary conditions (6) one obtains two additional equations

$$\frac{in\omega}{c_n k_n} J_1(k_n a) + \frac{\omega^2 n^2 a P^*_{\lambda n}}{2\mu c_n^2 k_n^2} = i\omega n \bar{U}^*_{\lambda n} \quad (21)$$

$$aJ_o(k_n a) - \frac{i\omega n P^*_{\lambda n}}{\mu c_n k_n^2} = i\omega n \bar{W}^*_{\lambda n} \quad (22)$$

Together with equations (19) and (20) these represent four equations for the determination of the unknowns. The speed of propagation c_n is obtained by setting the determinant equal to zero. From the above equations (19) through (22) the ratios $A_{\lambda n}/P^*_{\lambda n}$, $\bar{U}^*_{\lambda n}/P^*_{\lambda n}$ and $\bar{W}^*_{\lambda n}/P^*_{\lambda n}$ may be obtained, and are given as functions of the system parameters. Introducing these into the equations (7), (8), (9), (17) and (18) yields the results of the behavior of such a pulsating system, superimposed upon a uniform flow (14).

Results: The mathematical solution has been found for an arbitrarily pulsating flow superimposed upon a uniform flow. The speed

of propagation c_n is obtained by setting the coefficient determinant obtained from equations (19) through (22) equal to zero. With this the ratios $A_{\lambda n}/P^*_{\lambda n}$, $\bar{U}^*_{\lambda n}/P^*_{\lambda n}$ and $\bar{W}^*_{\lambda n}/P^*_{\lambda n}$ are obtained from these equations. The values $A_{\lambda n}$, $\bar{U}^*_{\lambda n}$ and $\bar{W}^*_{\lambda n}$ are therefore known for a given pressure.

Publication: "On the Shape of a Rotating Fluid System Consisting of a Gas Bubble Enclosed in a Liquid Globe," Zeitschrift fur Angewandte Mathematik und Physik. (Accepted for Publication)

Graduate Student: Ph.D. Candidate.

2. A Study of Helicopter Blade Slap Noise - R. B. Gray

Research Performed and Results Obtained: The interaction under certain flight conditions of a helicopter blade with the vortex field shed from preceeding blades produces a loud repetitive noise. Other studies have shown that a realistic mathematical model of the vortex structure is required for analysis of the noise generating mechanism. Such a model is not presently available. The objective of this grant is to explore several methods of measuring the flow field associated with vortex systems.

Thus far, a hot-wire anemometer has been used to study the flow field of vortex rings generated in air. By suitable orientation of the single wire, magnitudes of the total velocity and the axial velocity have been obtained across the vortex at a station 0.3 meters from the vortex generator exit. During this reporting period, a hot-film vector anemometer has been acquired which is capable of measuring the three velocity components simultaneously. The output of this vector

anemometer will be fed into a small digital computer for data reduction. The computer program has been written and checked out. The electronic interface including the analog to digital converters have also been designed, assembled, and checked out. It is conservatively estimated that the system is capable of a velocity vector sampling rate greater than ten thousand per second. This will be used for further study of the vortex ring.

The helicopter model rotor test facility is in the detail design stage. Construction is expected to begin in the near future.

A proposal has been written and submitted to NASA Langley to study vortex shedding from helicopter blades.

Graduate Student: M.S. Student.

3. Energy Conversion in Reactive Collisions - T. Moran

Research Performed and Results Obtained: As part of the program in High Energy Chemistry we have pursued the experimental and theoretical aspects of our investigations into the fundamental basis of energy conversion in reactive and non-reactive bimolecular collisions. Ion-molecule reactions have been examined in a significantly improved high resolution beam apparatus. Reactant ion beams are supplied by a small Nier type mass spectrometer. The ion beams from this spectrometer are focused into a 127° electrostatic energy selector which was fabricated from fine wire mesh grids of a design similar to those used in electron scattering experiments. The mass and energy selected ion beam is then focused into the collision chamber where reactions take place. Neutral

target molecules enter the collision region through a multichannel, fused capillary array which provides high target atom concentrations in a small, well defined region with a primarily monodirectional velocity distribution. This neutral beam, which intersects the ion beam in a perpendicular direction, is fed directly into a 3000-l/sec. diffusion pump. Ionic scattering products are measured in the out of plane dimension with a detection system consisting of another 127° sector, a Paul-Steinwedel mass filter and a channel electron multiplier. Channeltron signal pulses are amplified, shaped and then counted. The entire apparatus is mounted on an optical bench inside a 32 in. diameter stainless steel high vacuum chamber.

In ion-neutral molecule scattering processes, the kinetic energy of elastically scattered ions can be calculated from the expression

$$E_e = \frac{M^2 E_o}{(m+M)^2}\left[(2\cos^2\theta - 1) + \left(\frac{m}{M}\right)^2 \pm \frac{2m}{M}\cos\theta\left(1-\frac{M^2}{m^2}\sin^2\theta\right)^{1/2}\right]$$

where θ is the laboratory scattering angle, E_o is the energy of the incident ion of mass M and m is the mass of the target atom. For inelastically scattered ions a similar relation holds

$$E_i = \frac{M^2}{(M+m)^2} E_o\left[(2\cos^2\theta - 1) + \frac{m^2}{M^2}\left(1-\frac{\Delta E}{E_s}\right) \pm \frac{2m}{M}\left(1-\frac{\Delta E}{E_s}\right)^{1/2}\cos\theta\left(1-\frac{M^2\sin^2\theta}{m^2\left(1-\frac{\Delta E}{E_s}\right)}\right)^{1/2}\right]$$

where ΔE is the spectroscopic energy loss and E_e is equal to $mE_o/(m+M)$. The kinetic energy distribution of the primary ion beam approximates 0.04 eV FWHM which is sufficiently narrow to allow separation of the elastic and inelastic components of the scattered beam. A convenient measure of inelasticity, or degree of energy conversion, is given by $E_e - E_i$ which can be computed knowing the energy of the incident ion, masses of reactants, the scattering angle θ and ΔE computed from spectroscopic constants using the relation

$$\Delta E = hc\omega_e(\nu'-\nu) - hc\omega_e X_e\left[(\nu'+1/2)^2 - (\nu+1/2)^2\right] + (h^2/8\pi^2 I)\left[J'(J'+1) - J(J+1)\right]$$

where primed numbers refer to the final quantum states. The inelastic energy loss spectra for a typical interaction of the type

$$CO^+X^2\textstyle\sum(\nu,J) + Ar \rightarrow CO^+X^2\sum(\nu',J') + Ar$$

show that the majority of inelastically scattered product ions are forward scattered with positions approximating those from the computed values of $E_e - E_i$. Experimental points at large angles give evidence of rather sharp peaks due to inelastic collisions corresponding to vibrational excitations but at smaller angles there is significant broadening of these peaks and at nominal 0° LAB angle a maximum appears in the scattered intensity below the $\nu=0\rightarrow1$ threshold. Although a small amount of inelastic peak broadening is expected from the finite velocity width of the incident ion beam and small out of plane velocity components of

the target atoms; the experimental width of the inelastic peaks is larger than expected for pure vibrational transitions and gives indications of simultaneous vibrational and rotational excitations. As the reactant ion kinetic energy is lowered to 3 eV LAB energy, transitions with smaller energy losses become relatively more important and correspond to pure rotational excitations with changes in rotational quantum number, $\Delta J \approx 20$ for these large impact parameter collisions.

The relative differential cross sections measured for the vibrational excitations compare favorably with those predicted from a forced harmonic oscillator model with time dependent wavefunctions to evaluate transition probabilities. This model correctly predicts the relative $\nu = 0 \rightarrow n$ vibrational cross sections at given values of LAB scattering angles and the angular variation of these cross sections once the interaction potential has been determined.

The energy conversion processes involving chemically reactive species have been examined and it is found that a statistical model adequately describes total cross sections for various reaction channels as a function of incident ion translational energy. The cross sections for chemical rearrangement reactions of low energy C^+ ions with N_2 and O_2 leading to CN^+ and CO^+ respectively, are in reasonable agreement with the predictions of the statistical phase space model as regards translational energy dependences. However quantitative comparison between the results using this model and experimental data indicate that product states do not necessarily mix statistically and spin and symmetry requirements play a role in determining the product states. Translational energy dependences of dissociative reactions as determined from the

statistical model appear to be correct, but the statistical treatment overestimates the magnitude of this channel. Competing charge transfer processes with close energy balance between initial and final states, are better described by the nearest resonance model with the statistical approach limited to close coupled collisions where the electron transfer reactions have significant energy defects.

Publications: "Pure Rotational Excitation in CO^+ - Ar Interactions by Ion Beam Collision Spectroscopy," T. F. Moran, Frederick Petty and George S. Turner, Submitted to Chemical Physics Letters.

"Calculated Ion-Molecule Reactions of C^+ with O_2 and N_2," D. C. Fullerton and T. F. Moran, Submitted to International Journal of Mass Spectrometry and Ion Physics.

"Vibrationally Inelastic, Low Energy CO^+ - Ar Collisions," F. C. Petty and T. F. Moran, Submitted to Physical Review.

Papers Presented to Scientific Meetings: An invited paper "Vibrational Excitation in the Collisions of Atomic Ions with Neutral Molecules" will be presented in July at the Cambridge Conference on Molecular Energy Transfer, which is jointly sponsored by Cambridge University, England, and the U. S. National Academy of Sciences.

Graduate Students: Two Ph.D. Students.

4. Atomic and Magnetic Ordering in Transition Metal Alloys - S. S. Spooner

Summary of Progress: The electronic structure of the magnetic moments in the equiatomic alloys has been under investigation by polarized

neutron diffraction as a function of order and the metallurgical aspects of vanadium alloys additions have been under metallographic study in an attempt to understand the commercial practice of alloying the equiatomic alloys with 2% V. Recent band calculations for pure iron (Duff and Das, Phys. Rev. 3, 192 (1971)) provide important insights into the electronic structure which allow us to conclude that our results from Mossbauer spectroscopy and neutron diffraction experiments are consistent. The metallurgical question is far from being completely understood, but it can be suggested that interstitial impurity control and grain refinement effects due to vanadium may serve as an important additional factor in inhibiting brittle fracture tendency in the commercial FeCo alloy.

The polarized neutron diffraction experiments on polycrystalline alloys in the ordered and disordered condition give an indication of the changes in electron structure as a function of order. The magnetic electron form factors which are experimentally measured are related to the Fourier transform of the magnetic electron density and in other experiments on metals have been analyzed in terms of calculated form factors derived from free atom calculations by Watson and Freeman. In consideration of the fact that we are in fact dealing with atoms in the metallic state, it is very fortunate that the free atom calculations are found to be so useful. Our most recent efforts in data analysis show that the cobalt magnetic moment undergoes an apparent change in spacial distribution which is indicated by the fact that use of the Co^{+3} form factor in the ordered state and Co^{+1} form factor in the disordered state lead to the best data fit. The Fe^{+2} form factor appears

to apply in both ordered and disordered states. Using this kind of form factor analysis, it is found that the localized magnetic moments on iron or on cobalt do not change as drastically as we first thought. However, the unlocalized magnetization is negatively polarized and decreases in magnitude upon ordering. (This determination is based on demanding a consistency between bulk magnetization and localized magnetization determined in the neutron scattering experiments.)

In addition to assessing the magnitude of moments, we obtained a measure of the non-spherical distribution of the local moment electrons which is due to the cubic crystalline field. The degree of asphericity observed in the magnetic electron form factors was comparable to the asphericity observed in pure iron and was not a function of order in the alloy.

The changes in the magnetic electron structure are indicated in Mossbauer spectroscopy through changes in hyperfine field and changes in polarized electron density at the iron nucleus giving an isomer shift. The decrease in the negative magnitude of the hyperfine field upon ordering is consistent with our neutron observations of the moment changes using the view that the dipolar effects of the cobalt moment at the iron nucleus play the prominant role. However, the negatively polarized non-localized moment was found to decrease in magnitude upon ordering, making it difficult to explain the change of isomer shift with ordering which would call for an increase in negatively polarized electron density at the nucleus. It has been suggested by many that the non-localized electrons were s-like in character. However, the calculations for pure iron by Duff and Das appear to offer a means for rationalizing

our observations. They show that the negative magnetization density associated with non-local electrons is found in outlying regions of the atomic cell and is due to spin dependence of the radial part of the d-electron wave functions. Furthermore, there appears to be no mechanism for negative polarization of the 4-s electron wave function in iron. Thus, no direct connection between non-localized moment and 4-s electron wave functions is required by their model of electron behavior for iron.

The further analysis of the ordering changes upon the electronic structure through magnetic electron behavior appears to be a promising approach.

The metallurgical aspects of alloying additions to iron-cobalt in order to control brittleness have been controversial for some time. On one hand, it has been advocated that control of ordering by alloying additions was principally responsible for mechanical property improvement. On the other hand, interstitial impurity effects on embrittlement are thought to be controlled by vanadium as a gettering agent. It would be surprising if both views were not correct in some degree.

The effect of carbon in the iron-cobalt system was put under study since carbides can play an important role in brittle fracture. A pure iron, an iron-cobalt, and a commercial Fe-Co-2%V alloy were carburized at 950°C and then rapidly cooled and metallographically polished to reveal carbide structure. While the treatment was in no way representative of industrial practice to our knowledge, it afforded a convenient means for examining carbide behavior in iron-cobalt and iron-cobalt alloys. Two features in this study were revealed metallographically:

1) carbide formation morphology differences, and

2) vanadium carbide inhibition of grain growth and cementite growth.

The vanadium carbide precipitation at austenite grain boundaries as well as within grains appeared to confine carbide formation to a continuous mode of precipitation (as distinguished from a discontinuous-cellular mode). Small austenite grain size was preserved in the vanadium containing alloy while a larger grain size in both iron and iron-cobalt developed in the early stages of carburization treatment. The mode of carbide precipitation in Fe-Co was distinctly different from the well known pearlite formation, but macroscopically resembled a plate-like growth with irregular though nearly parallel boundaries between the body-center cubic ferrite and carbide cementite.

It is known that cobalt carbide is highly unstable and that graphite precipitation is favored in cobalt containing alloys. With this in mind we were interested in learning whether cobalt was equally partitioned between the ferrite and carbide. Our microprobe studies are not complete although it can be anticipated that in the first of our experiments with rapid formation of carbide, substitutional diffusion would not allow much adjustment of cobalt content in the carbide. Nevertheless, it is interesting to note that the mode of carbide formation is distinctly different between the iron and the iron-cobalt case. Whether this is due to an increase in the eutectoid temperature with cobalt additions (carbide precipitation starting temperature) or due to cobalt partitioning effects or due to changes in bulk and surface thermodynamic properties of the carbide is not certain.

In retrospect, our investigations have pointed out that carbide formation with vanadium will tie up carbon in a form that will prevent graphite flake formation, reduce interstitial embrittlement and inhibit grain growth. All these factors militate against brittleness and brittle fracture tendency.

Publication: "Magnetic Scattering of Neutrons by Equiatomic FeCo in the Ordered and Disordered State," by J. W. Lynn, S. Spooner and J. W. Cable, to appear in Solid State Division Report of the Oak Ridge National Laboratory (1971).

Graduate Students: Two Ph.D. Candidates.

5. The Physical and Functional Aspects of Integrated-Circuit Technology - K. L. Su and D. C. Ray

Research Performed: In the circuit phase, further work has been done in the synthesis of active networks using the positive impedance converter (PIC), resistors, and capacitors. The results of the investigation of RC-PIC synthesis can be summarized in the following theorems:

Theorem 1

For the realization of an arbitrary N x N matrix of real rational functions in the complex frequency variable as a short-circuit admittance matrix of a transformerless active RC N-port network, (a) it is, in general, necessary that the network contains N PIC's; and (b) it is sufficient that the network contains N PIC's embedded in a 3N-port RC network.

Theorem 2

For the realization of an arbitrary N x N matrix of real rational functions in the complex frequency variable as a short-circuit admittance matrix of a transformerless grounded active N-port RC network, it is sufficient that the network contains 2N PIC's embedded in a (4N+1)-terminal RC network.

Theorem 3

An N x N matrix of real rational functions in the complex frequency variable having L simple poles on the negative real axis in the complex frequency plane and no more than L+1 zeros can be realized as a short-circuit admittance matrix of a transformerless active network having no more than N PIC's embedded in a 2N-port RC network.

Theorem 4

An N x N matrix of real rational functions in the complex frequency variable having L simple poles on the negative real axis in the complex frequency plane and no more than L+1 zeros can be realized as a short-circuit admittance matrix of a transformerless grounded active network having no more than 2N PIC's embedded in a (3N+1)-terminal RC network.

Theorem 5

For the realization of an arbitrary N x N matrix of real rational functions in the complex frequency variable as a voltage transfer matrix of a transformerless active RC 2N-port network, (a) it is, in general, necessary that the network contains N PIC's; and (b) it is sufficient that the network contains N PIC's embedded in a 3N-port RC network.

Theorem 6

For the realization of an arbitrary N x N matrix of real rational functions in the complex frequency variable as a voltage transfer matrix of a transformerless grounded active RC 2N-port network, it is sufficient that the network contains 2N PIC's embedded in a (4N+1)-terminal RC network.

The results of the investigation on stability criteria reveals that if one port of a terminated PIC is open-circuit stable (OCS) and short-circuit stable (SCS), the other port must also be OCS and SCS. The conditions for the terminated PIC to be OCS and SCS are imposed on the dynamic gains of controlled sources in the PIC, which can easily be satisfied from practical points of view.

The study of the sensitivity in the RC-PIC networks with respect to the current-conversion-gain change in the PIC can be reduced drastically as compared to those in RC networks with the negative impedance converters, while sensitivities with respect to the voltage-conversion-gain change in the PIC increase slightly.

In the device phase, work has been centered on the assembly of an rf sputtering station utilizing an NRC oil diffusion pump (NHS4) fitted with a liquid nitrogen cryobaffle. Several difficulties were resolved in developing an operational system capable of sputtering semiconductor films at argon pressures of two microns.

A series of Ge films were sputtered using freshly cleaved CaF_2 as the substrate material. Electron diffraction studies indicated that good single crystal films had been obtained at substrate temperatures of 400°C. This suggests that the surface and its preparation

rather than the gross deposition parameters of the rf sputtering process itself are the major obstacles to obtaining epitaxy on sapphire.

This line of reasoning led to the design and construction of a novel substrate platform for sputter cleaning either conducting or insulating substrates. The required negative bias of a few hundred volts was developed by separate excitation at 7 MHz in order that cleaning might take place at any stage of the primary target sputtering process. The platform also incorporated a graphite cloth radiant heater and a radiantly heated thermocouple for measuring substrate temperature. A tuning network was constructed to match the glow discharge impedance of the platform to the rf exciter output impedance.

The analysis of the eddy current method of measuring film conductivity at microwave frequencies was extended to include the effects of the substrate. An Algol program was written and computations were made for germanium films on calcium fluoride and sapphire substrates. The surprising dependence of the film dissipated power upon the substrate thickness appeared to be substantiated by data from earlier experimental measurements. However further analytical and experimental investigations are required to exploit the significance of these results.

Publication: N. W. Cox, Jr., K. L. Su, and R. P. Woodward, "Operational-Amplifier Realization of the Nullor and the Universal Impedance Converter," to appear in IEEE Transactions on Circuit Theory, May 1971.

Graduate Students: Three Ph.D. Candidates.

6. Collisional De-excitation of Atomic Particles - E. W. Thomas

Research Performed in the Current Period: Work has been concentrated on the study of the cross section differential in angle for the charge transfer process. Work is principally directed at targets of helium where a theoretical understanding should be tractable; however, empirical data has also been obtained for more complex targets of practical interest.

It appears that the proportion of the neutrals formed in the 2s state is a very sensitive function of scattering angle; excited state fractions of 10% have been recorded at large angles. The proportion of metastable neutrals rises from about 1% at zero scattering angle to 10% at one degree of arc or greater angles; the rise is very rapid and occurs at approximately the same impact parameter for all impact energies. Some qualitative understanding of this phenomenon in the case of H^+ impact on He may be achieved by inspection of the potential energy curves of the $(H\ He)^+$ molecule. At the internuclear separation where the rise in probability of metastable formation occurs, one finds a fairly rapid change in the relative separation of certain important potential energy curves. At greater separations the curve for H(2s) lies much higher in energy than H(1s), implying that H(1s) formation is the most likely neutral atom formation mechanism; thus small angle scattering which must involve large internuclear separation gives rise to small probabilities of metastable formation. In contrast, at small internuclear separations the curves for H(1s) and H(2s) are very close together and one expects only small differences in cross sections for the formation of these levels; this again is consistent with the

observation that large angle scattering, which inevitably involves small internuclear separations, gives rise to a population of the metastable state that is of the same order as ground state population. While the considerations give qualitative explanations of the observed behavior, a quantitative understanding has not yet been properly developed.

The phenomena described for charge transfer in helium are repeated in the same general manner when considering heavier, more complex gas targets. In these cases, however, a detailed understanding is more difficult due to the non-availability of accurate potential curves.

The experiments have also yielded general information on scattering cross sections that may be correlated with a Rutherford type theoretical formulation and utilized to derive an effective potential for the interaction of the colliding atoms. Use of screened Coulomb potentials provides a rather good prediction of the cross section for the scattering of all particles into some definite angle.

A detailed study has also been made of processes whereby H_2^+ is dissociated and H(2s) formed. In this case one has three or more particles participating in the collision; the description of potential energy must be detailed in terms of a family of surfaces. The dissociation problem is rather complex. Here again it is observed that a small proportion of metastable neutrals is produced in small angle scattering and a large proportion at large angles. The detailed angular distribution can in part be predicted in terms of the potential energy liberated in the frame of reference of the dissociating molecule.

The work on this project will continue with particular emphasis on the study of complex target systems (O_2, N_2 and possibly O) and further studies also made on the processes whereby H(2s) is collisionally destroyed.

Publications: "Formation of Metastable Hydrogen Atoms by Charge Transfer," by R. L. Fitzwilson and E. W. Thomas will be published in the "Physical Review" (April 1971).

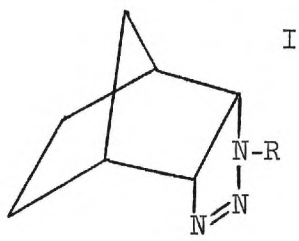
"Differential Cross Sections for the Formation of Metastable Hydrogen by Charge Transfer," by E. W. Thomas and R. L. Fitzwilson has been published in the "Bulletin of the American Physical Society" (Volume 15, page 1504, 1971).

Paper Presented to Scientific Meetings: A paper entitled "Differential Cross Sections for the Formation of Metastable Hydrogen by Charge Transfer" was presented at the "Annual Meeting of the Division of Electron and Atomic Physics of the American Physical Society" in Seattle (November 1970).

Graduate Students: Two Ph.D. Candidates.

7. Studies in Nitrene Chemistry - L. H. Zalkow and C. L. Liotta

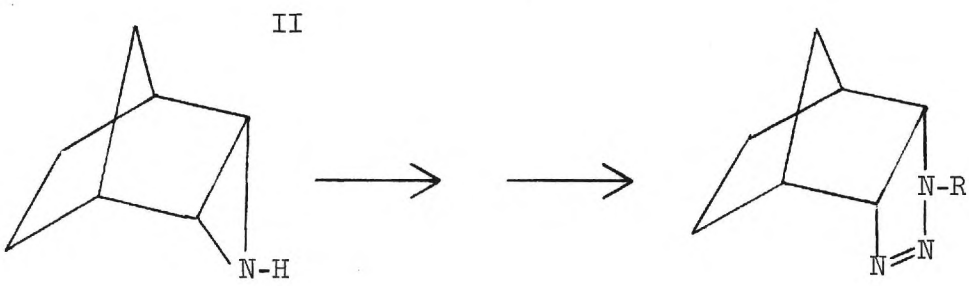
Introduction: The goal of this problem is to prepare an endo-triazoline of the bicyclo [2,2,1] System as shown.



I

In the past there have been several attempts to prepare this type of compound. To date there has been reported only one success in which phenyl azide was added to norbornene[1]. The endo adduct was prepared in low yield and was isolated via fractional crystallization from the exo isomer. A better method has yet to be reported.

Our approach to this problem is to first prepare the unsubstituted endo-aziridine II in good yield and then convert this to the desired triazoline.



There have been many attempts to add electrophilic reagents (INCO, IN_3, etc.) to norbornene in hopes to incorporate a nitrogen containing functional group endo. These have not worked at all.

There seems to be several alternatives to the above procedures. First is incorporation of the nitrogen function in the molecule at the start. Secondly, to block the exo- attack of certain reagents by placing a hindering group on the C_7 carbon syn to the double bond in norbornene. Thirdly, a sequence of reactions to convert some nitrogen function on the norbornane skeleton to an endo nitrogen functional group.

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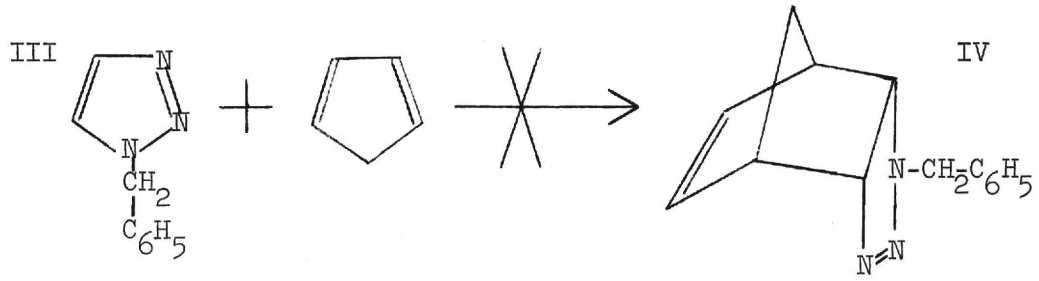
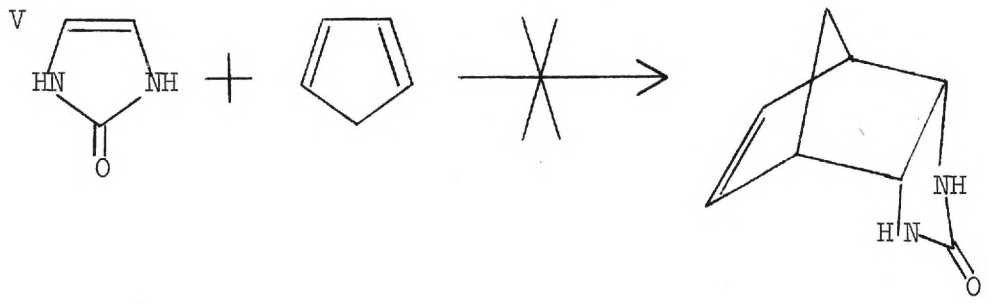
[1] S. McLean & D. M. Findlay, Tet. Letters, #27, 2219 (1969).

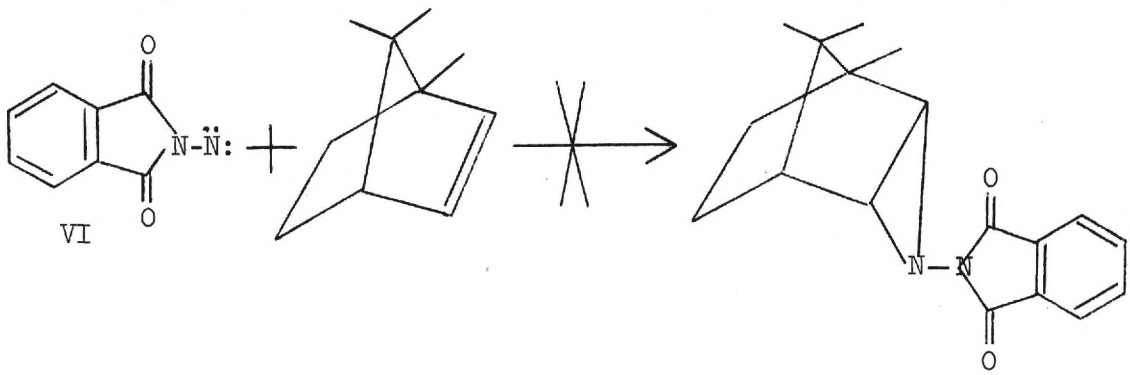
Experiments: The triazole III was prepared and attempts were made to react this with cyclopentadiene in hopes that the endo triazoline IV would form. The triazole failed to react.



The imidazolone V was prepared and attempts were made to react this with cyclopentadiene. The starting imidazolone was recovered unchanged.

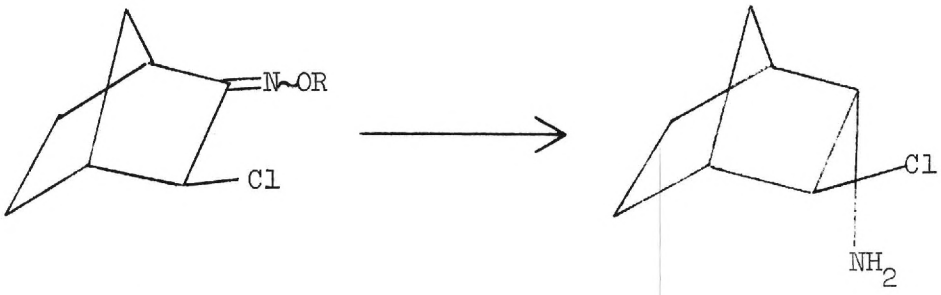


In still another attempt the nitrene VI formed from treatment of N-amino phthalimide with lead tetraacetate was added to bornylene.



There was no adduct formed.

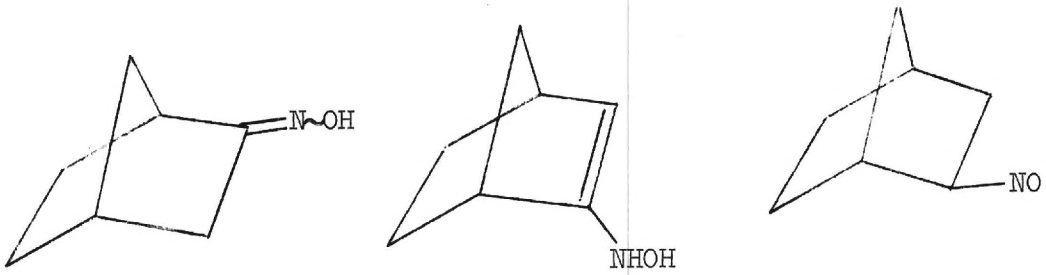
At present the best approach which is being developed in the preparation of the chlorooxime VIIa and subsequent reduction to the amino compound VIII.



VII
a,R = H
b,R = Ac

VIII

The reaction of VIIIb with $NaBH_4$ in methanol gives the dehalogenated and reduced products IX and X or XI.



IX X XI

Catalytic reduction with Rh on carbon is presently being pursued. Although no products have been identified, the resulting products seem to have been dehalogenated.

Graduate Students: Two Ph.D. Candidates.

III. CONCLUSIONS

The NASA Multidisciplinary Grant NGL 11-002-018 continued to stimulate research on the campus and its effectiveness is demonstrated by the number of publications (5), submissions (3) and presentations (2) during the six month period, September 15, 1970 to March 14, 1971.

Through the grant graduate students are engaged in quality research activities and students in the following categories received financial support from the grant: M.S. - 1 and Ph.D. - 12.